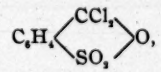
VOL. XXX. OCTOBER, 1903. NO. 4.

AMERICAN CHEMICAL JOURNAL

FURTHER INVESTIGATIONS ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

Since the last communications on this subject[1] work has been continued somewhat interruptedly, as other matters have claimed attention. That two isomeric chlorides of orthosulphobenzoic acid exist has been shown beyond any possibility of doubt. The relations between these chlorides have perhaps not yet been made entirely clear, but the study of the reactions of the two with a number of substances has brought to light many facts of interest that must be taken into account in dealing with the problem of isomerism presented by the chlorides. List and Stein[2] have shown that the substance described by Saunders[3] and myself, and later by McKee,[4] and myself and believed to be the pure unsymmetrical chloride,



with the melting-point 21° to 22°, is in reality "a mixture"

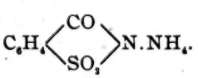
[1] This JOURNAL, 18, 791, 794, 809, 819.
[2] Ber. d. chem. Ges., 31, 1648.
[3] This JOURNAL, 17, 352.
[4] *Ibid.*, 18, 794.

of the chloride melting at 79° and another melting at 40°. This "mixture" has a constant melting-point that is not changed by repeated crystallizations. It crystallizes in definite form and presents the characteristics of a definite chemical compound. List and Stein also observed that the melting-point is not changed "durch wiederholtes Krystallisiren." The low-melting chloride used in the work treated of in the following articles was prepared by the method of List and Stein.

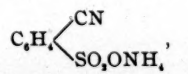
The work has been extended to a nitro derivative of orthosulphobenzoic acid that happens to be comparatively easily obtainable. The corresponding isomeric chlorides containing the nitro group have been prepared and their reactions studied,[1] and the chlorides of parabromorthosulphobenzoic acid have been prepared and investigated. The results of this work will soon be communicated. The main point of interest connected with all this work is the peculiar character of the relation between the isomeric chlorides. Each one of any given pair of isomers is a definite substance with well-defined properties. One cannot be transformed into the other by any means thus far employed. If one is dissolved in any solvent that does not act chemically upon it, that one comes out of the solution again, and it retains its identity after repeated crystallizations. Nor can one be transformed into the other by heat. So far as the substances themselves are concerned, there is no reason for calling one the *stable* and the other the *unstable* variety. In their relations towards other substances, on the other hand, a marked difference is observed. The chloride of higher melting-point enters into reaction much less readily than that of lower melting-point. Hence, List and Stein[2] propose to call the former the *stable* and the latter the *unstable* chloride. As I have previously pointed out, it seems highly probable that one of the chlorides contains the group $C_6H_3(COCl)(SO_2Cl)$ and the other the group $C_6H_3(CCl_2)(SO_2)O$; and, accordingly, I have called the one containing the former

[1] Remsen and Gray: This JOURNAL, 19, 496; Hollis: *Ibid.*, 23, 233.
[2] *Loc. cit.*

group the *symmetrical*, and the one containing the latter group the *unsymmetrical* chloride. I have also shown that the reactions of the chloride of orthosulphobenzoic acid that melts at 79° make it probable that this is the symmetrical variety, and the weight of evidence is also in favor of the conclusion that the chloride with the lower melting-point is the unsymmetrical variety. It must be confessed that the case is a difficult one to deal with, for the reason that, with some reagents, both chlorides give the same products, and these sometimes have the symmetrical and sometimes the unsymmetrical structure. If this were true of all reagents, the task would plainly be a hopeless one. List and Stein[1] hold that the facts do not justify any conclusion in regard to the structure of the chlorides. I still think that my former conclusions are justified. The reactions upon which I have relied are those with ammonia and those with aniline and similar bases. List and Stein agree with me in regard to the action of ammonia. It is established that the chloride melting at 79° reacts with ammonia in such a way as to form quantitively the ammonium salt of benzoic sulphinide,



On the other hand, the chloride with the lower melting-point, treated with the same reagent, yields principally the ammonium salt of orthocyanbenzenesulphonic acid,

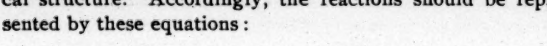


together with a greater or smaller quantity of the ammonium salt of benzoic sulphinide. The quantity of the latter product depends upon the temperature. The lower the temperature the smaller the quantity. Under some conditions the ammonium salt of *o*-cyanbenzenesulphonic acid is the sole product, not even a trace of the sulphinide being formed.

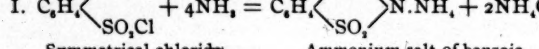
The above facts, taken by themselves, lead clearly to the

[1] *Loc. cit.*

conclusion that the chloride melting at 79° has the symmetrical structure, and that the other chloride has the unsymmetrical structure. Accordingly, the reactions should be represented by these equations:



Symmetrical chloride. Ammonium salt of benzoic sulphinide.



Unsymmetrical chloride. Ammonium salt of orthocyanbenzenesulphonic acid.

The action of ammonia on the two chlorides has been further investigated in this laboratory by Mr. R. M. Bird. In general, the earlier results have been confirmed. The unsymmetrical, or high-melting, chloride gives only the sulphinide. The pure, unsymmetrical, or low-melting chloride gives mainly the ammonium salt of *o*-cyanbenzenesulphonic acid with more or less of the ammonium salt of benzoic sulphinide, depending upon the conditions of the experiments. When very dilute (1 : 20) aqueous ammonia was used the reaction took place very slowly and only a trace of the sulphinide was obtained. This was detected by the taste and could not be isolated. With stronger ammonia (1 : 3) the amount of sulphinide obtained formed from 4 to 20 per cent of the total product. About the same results were obtained when the most concentrated ammonia was used. On the other hand, when the chloride was dissolved in anhydrous ether or chloroform, and dry ammonia gas passed into the solution, only the ammonium salt of *o*-cyanbenzenesulphonic acid was obtained. The product did not have a sweet taste, a fact that shows conclusively that not even a trace of the sulphinide was formed.

The further study of the action of alcohols upon the two chlorides which has been carried out by Mr. R. M. Bird has confirmed the results previously obtained and has brought to light some facts not heretofore established. The principal

facts to be noted in this connection are these, that the high-melting chloride yields acid esters with alcohols,

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 2ROH = C_6H_4\begin{cases}COOR\\SO_2OH\end{cases} + HCl + RCl,$$

while the low-melting chloride yields, first, ester chlorides, and these in turn give the acid esters:

$$\text{I. } C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O + ROH = C_6H_4\begin{cases}COOR\\SO_2Cl\end{cases} + HCl;$$

$$\text{II. } C_6H_4\begin{cases}COOR\\SO_2Cl\end{cases} + ROH = C_6H_4\begin{cases}COOR\\SO_2OH\end{cases} + RCl.$$

It appears, however, that when the high-melting chloride, in solution in anhydrous ether, is treated with a solution of sodium ethylate in ethyl alcohol the ester chloride is formed,

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + NaOC_2H_5 = C_6H_4\begin{cases}COOC_2H_5\\SO_2Cl\end{cases} + NaCl,$$

though this reaction requires further study.

In regard to the reactions with aniline, List and Stein state that they worked exactly as we did, but obtained different results.

In an earlier article by Kohler and myself[1] it is stated that (1) "the product of the action of aniline upon the dry, high-melting chloride is symmetrical orthosulphobenzanil, which has the structure represented by the formula

$$C_6H_4\begin{cases}CO\\SO_2\end{cases}NC_6H_5;"$$

(2) that "the product of the action of aniline upon the solid chloride in an emulsion with water is symmetrical orthosulphobenzanilide, which has the structure

$$C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases};"$$

[1] This JOURNAL, 17, 330.

and (3) that "the product of the action of aniline upon the liquid (low-melting) chloride of orthosulphobenzoic acid is the infusible anilide."

Later, McKee[1] repeated the experiments of Kohler and found that the high-melting chloride gives only the anilide of the structure $C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}$, and none of the infusible anilide. He found, however, that the low-melting chloride used by him (melting at 21° to 22°) gives both anilides.

Evidence has previously been presented that goes to show that the anilide obtained from the high-melting chloride is the symmetrical one represented by the formula

$$C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}.$$

As the other anilide was not obtained from this chloride, it was concluded that the high-melting chloride has the symmetrical structure as indicated by the reaction with ammonia. The fact that two anilides, or, at least, two substances of the same composition as the anilide are formed from the low-melting (liquid) chloride, appears to be analogous to the fact that two isomeric products are formed when ammonia and water act upon this same chloride.

On treating a mixture of the two chlorides with aniline some of the anil was always formed.

The main fact that appeared to be established by these earlier investigations is the formation of the symmetrical anilide alone from the high-melting chloride. List and Stein state that each of the chlorides gives all three of the products above referred to, that is to say, the symmetrical anilide, the unsymmetrical anilide, and the anil. If this be true, my former argument based on the action of the chlorides towards aniline is of no value.

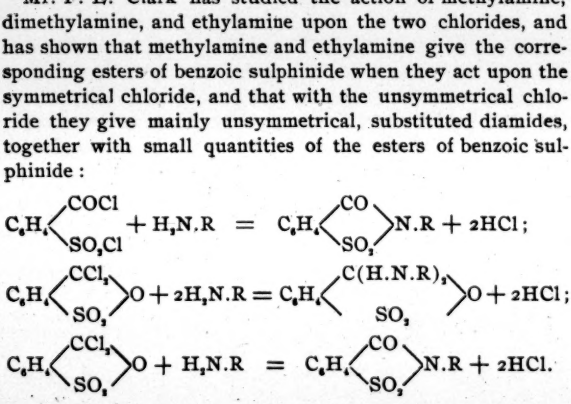
Though feeling certain that there was no error in my work, I have repeated it with the aid of Mr. W. B. Holmes, and have found that when the high-melting chloride is treated

[1] This JOURNAL, 18, 804.

with aniline in the presence of water no trace of the unsymmetrical anilide is formed, the products being the symmetrical anilide and the anil. On the other hand, when the low-melting chloride is treated in the same way, the products are the two anilides and no anil.

If, however, either of the chlorides is dissolved in ether and then treated with aniline, all three of the products already referred to are formed as claimed by List and Stein. The method employed by us consists in adding the aniline to an emulsion of the chloride in a relatively large amount of cold water. Reaction then takes place without perceptible evolution of heat.

Mr. F. E. Clark has studied the action of methylamine, dimethylamine, and ethylamine upon the two chlorides, and has shown that methylamine and ethylamine give the corresponding esters of benzoic sulphinide when they act upon the symmetrical chloride, and that with the unsymmetrical chloride they give mainly unsymmetrical, substituted diamides, together with small quantities of the esters of benzoic sulphinide:

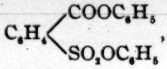


He has shown, further, that with dimethylamine the high-melting chloride gives a symmetrical product, or at least that only one product is formed, and this has presumably the symmetrical structure. The low-melting chloride, on the other hand, does not give a definite product when treated with dimethylamine.

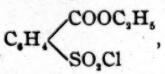
List and Stein,[1] in studying the action of phenol upon the two chlorides, deny the correctness of the statements of Rem-

[1] *Loc. cit.*

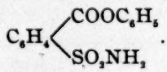
sen and McKee[1] to the effect that when the symmetrical chloride is treated with phenol the diphenyl ester,



and the phenyl ester chloride,

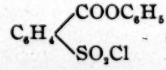


are formed. The existence of the latter in the product was not shown by isolating it, but by treating the mass with ammonia, when the chloride was converted into the phenyl ester of *o*-sulphaminebenzoic acid,



List and Stein were unable, for some reason, to obtain this compound and they make the following sweeping statement in regard to it: "Hingegen, haben wir uns trotz der sorgfältigsten Versuche vergeblich bemüht, den von Remsen dargestellten *o*-Sulfaminbenzoësäureester zu fassen. Nach unseren Versuchen scheint der Ester überhaupt nicht existenzfähig zu sein."

The work of Remsen and McKee has been repeated by Mr. R. E. Humphreys and the results confirmed. It is true that the sulphone chloride,

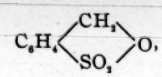


does not react with ammonia directly, but when a mixture of the symmetrical chloride and phenol is treated with ammonia the phenyl ester of *o*-sulphaminebenzoic acid is easily formed and is identical with the substance described under this name by Remsen and McKee. The low-melting chloride gives the same products with phenol as the high-melting chloride.

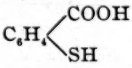
Mr. K. G. Falk has repeated the work of List and Stein on the reduction of the two chlorides and has obtained the same

[1] This JOURNAL, 18, 794.

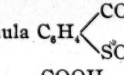
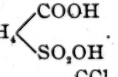
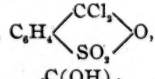
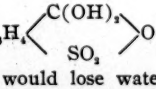
results. It is undoubtedly true that the high-melting, or symmetrical, chloride gives sulphobenzid,

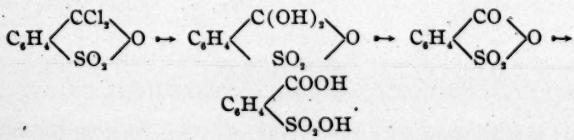


when reduced, while the low-melting, or unsymmetrical, chloride gives thiosalicylic acid,



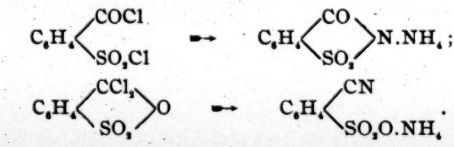
The reactions that must be taken into consideration in speculating upon the structure of the two chlorides are those with water, alcohols, phenols, ammonia, the substituted ammonias, and nascent hydrogen.

1. Water gives but one product, orthosulphobenzoic acid, whether the high-melting or the low-melting chloride is used. This is quite in accordance with what we should expect. A compound of the formula  would, of course, give one of the formula  . A compound of the unsymmetrical structure,  , would first give a product of the structure  . This is probably an unstable form which would lose water and yield the anhydride as an intermediate product. But this would at once take up water and form the acid. The changes involved are indicated below:



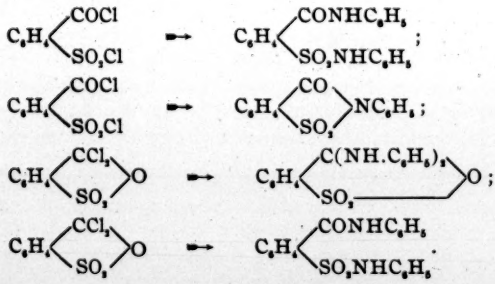
The action of water, therefore, throws no light upon the problem of the structure of the two chlorides.

2. The action of ammonia upon the two chlorides is of especial interest. Under proper conditions, the high-melting chloride gives only the ammonium salt of the sulphinide, and the low-melting chloride gives only the ammonium salt of *o*-cyanbenzenesulphonic acid :



These reactions are unequivocal and, if taken by themselves, show clearly that the high-melting chloride has the symmetrical, and that the low-melting chloride has the unsymmetrical, structure.

3. The reactions with aniline are not quite as clear as those with ammonia, but in general terms they confirm the conclusion to which those with ammonia point. An emulsion of aniline in cold water gives, with the high-melting chloride, the symmetrical anilide and the anil, while, under the same circumstances, the low-melting chloride gives the unsymmetrical anilide and the symmetrical anilide :

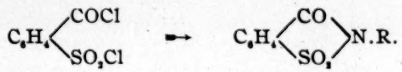


In the case of the unsymmetrical chloride, the proportion of

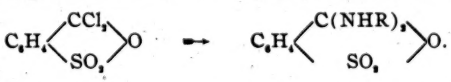
the unsymmetrical anilide formed is considerably larger than that of the symmetrical anilide.

These facts are in accordance with the view that the high-melting chloride has the symmetrical structure, and the low-melting chloride the unsymmetrical structure. The formation of the symmetrical anilide, together with the unsymmetrical anilide, from the low-melting chloride, is a symptom of a general tendency possessed by this chloride to yield, to some extent, symmetrical products.

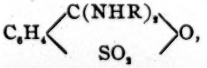
4. The action of methyl- and ethylamines and of dimethylamine is of the same general kind as that of aniline, though with some differences, as has been pointed out. The high-melting chloride gives esters of benzoic sulphinide with methyl- and ethylamines:



The low-melting chloride gives a diamide which is probably analogous to the infusible unsymmetrical dianilide:



This reaction furnishes no evidence for or against the formulas of the two chlorides, as it has not been proved that the product above represented by the formula



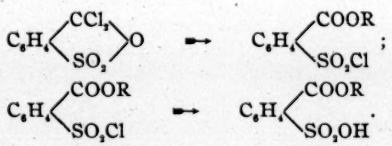
really has the unsymmetrical structure. To be sure, it is infusible like the unsymmetrical dianilide, but that is not strong evidence of its structure.

5. With alcohols the high-melting chloride does not react easily in the cold. When the solution is boiled or allowed to stand for some time the product is the acid ester:

By treating an alcoholic solution of the high-melting chloride with an alcoholic solution of sodium ethylate an ester chloride is formed :

The same reaction takes place with sodium methylate.

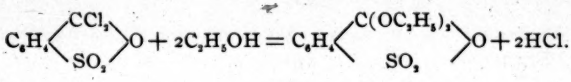
On the other hand, the low-melting chloride reacts very readily with alcohols and gives the ester chlorides which, by further action of the alcohols, give the acid esters :



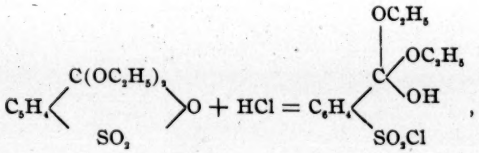
Both chlorides then give the same products with alcohols and these products have the symmetrical structure. To be sure, the symmetrical chloride with an alcohol alone does not give the intermediate ester chloride, but gives the acid ester. This appears to be due to the fact that this chloride reacts with difficulty with the alcohols. It is necessary to boil the solution and then, of course, the product is the acid ester, for, if the ester chloride were first formed, it would, under the conditions of the experiment, be converted into the acid ester. When, however, the reaction is aided by the addition of sodium alcoholate, the ester chloride is first formed.

The fact that ester chlorides are easily obtained from the low-melting chloride by treating them with alcohols, when taken by itself, suggests that this chloride has the symmetrical structure. But the fact cannot be taken by itself. The low-melting chloride has certainly not the same structure as the high-melting chloride and the evidence in favor of the symmetrical structure for the latter seems to me to be conclusive. It is clear, however, that the low-melting chloride with some reagents gives symmetrical products, though it generally gives unsymmetrical products.

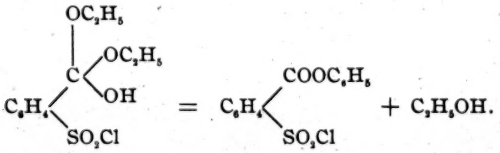
The formation of ester chlorides from a substance of the unsymmetrical structure is, further, easily accounted for without assuming any mysterious "molecular rearrangement." The first action of the alcohol is probably that represented by the equation



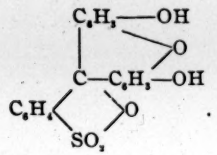
The anhydride would then take up hydrochloric acid:



and the product thus formed would lose alcohol and give the ester chloride

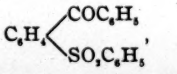


6. With ordinary phenol the reactions are somewhat different from those with the alcohols. It gives the same products with both chlorides. These are the phenyl ester chloride, $C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases}$, and the diphenyl ester, $C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases}$. Plainly no light is thrown upon the structure of the two chlorides by these reactions. Curiously enough, with resorcinol both chlorides give the same unsymmetrical product, sulphonfluorescein:

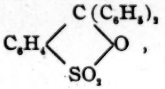


These reactions also do not help to determine the structural relations of the two chlorides.

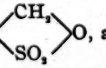
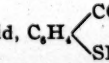
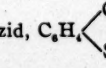
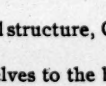
7. With benzene and aluminium chloride both chlorides give the same symmetrical product,



but under some conditions the low-melting chloride gives a little of another product, probably the isomeric, unsymmetrical compound,



though this is by no means certain.

8. The reduction of the two chlorides seems at first sight to show that the high-melting chloride is unsymmetrical and the low-melting chloride symmetrical. The high-melting chloride gives sulphobenzid,  , and the low-melting chloride gives thiosalicylic acid,  . If these were the only facts to guide us, we should probably conclude that the chloride that yields sulphobenzid,  , by reduction must have the symmetrical structure,  , and we could easily reconcile ourselves to the belief that the chlo-

ride that yields thiosalicylic acid, $C_6H_4\begin{cases}COOH\\SH\end{cases}$, must have the symmetrical structure, $C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}$, though this connection does not appear as clear as that between sulphobenzid and the unsymmetrical chloride.

It seems to me, however, that all the other reactions are more easily explained by assuming that the high-melting chloride is symmetrical and the low-melting chloride unsymmetrical. The question then naturally suggests itself: Can the reactions of the two chlorides with reducing agents be explained in any other plausible way than that adopted by List and Stein and outlined above? I think they can, and, indeed, I think the other explanation is, to say the least, fully as rational as that given by List and Stein. Take first a compound of the symmetrical structure, $C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases}$. It is well known that the group COCl is more easily reduced than the group SO_2Cl. We should, therefore, expect that the symmetrical chloride would first yield an aldehyde and then an alcohol, thus:

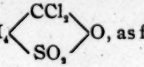
$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} \rightarrow C_6H_4\begin{cases}COH\\SO_2Cl\end{cases} \rightarrow C_6H_4\begin{cases}CH_2OH\\SO_2Cl\end{cases}.$$

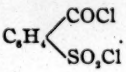
The alcohol would, however, easily lose hydrochloric acid and give the corresponding anhydride, sulphobenzid,

$$C_6H_4\begin{cases}CH_2\\SO_2\end{cases}O.$$

According to this the formation of sulphobenzid from the symmetrical chloride is not only possible but at least as probable as its formation from a chloride of the unsymmetrical structure.

Turning now to the reduction of the unsymmetrical, or low-melting, chloride. The product is thiosalicylic acid. How

can the formation of this substance be explained on the assumption that the chloride has the unsymmetrical structure? The low-melting chloride reacts very easily with water as with most other reagents. It seems probable that before the reduction could be effected the chloride would be converted partly into the anhydride and partly into the acid. The reduction of these would then, in turn, be likely to give thiosalicylic acid. An attempt was made to test this view experimentally, and apparently small quantities of thiosalicylic acid were obtained when the anhydride and the acid were reduced. The results were, however, not very satisfactory. Not much, if any, weight can be attached to these experiments. But, leaving them entirely out of consideration, it seems to me that it is as easy to explain the formation of thiosalicylic acid from a chloride of the formula  , as from one of the formula



The details of the experimental work are given in the following articles.

I. THE ACTION OF AMMONIA AND OF ALCOHOLS AND ALCOHOLATES UPON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

By R. M. Bird.

The action of aqueous ammonia of various dilutions and at various temperatures upon the low-melting chloride was first studied, and also the action of the dry gas upon solutions of the chloride in anhydrous ether and chloroform, as well as upon the dry chloride.

Very Dilute Aqueous Ammonia.—The solution was made by adding 20 volumes of water to 1 volume of a solution thoroughly saturated with ammonia at the temperature of hydrant water, about 18° C. The unsymmetrical chloride, either in

[1] From the author's dissertation submitted, June, 1901, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

solution in ether or dry, was treated with this ammonia at 0° and at the ordinary temperature. Two experiments were conducted at the former and four at the latter temperature. In all cases it required four or five days to complete the reaction, regardless of the amounts of chloride used, provided, of course, proportional quantities of ammonia were added. The products were, in all cases, ammonium orthocyanbenzenesulphonate, a trace of the ammonium salt of benzoic sulphinide and ammonium chloride. The cyanbenzenesulphonate was practically the only organic product of the reaction, for the amount of sulphinide was too small to be detected except by a slightly sweet taste of the solution. In no case could a precipitate be obtained on acidifying with hydrochloric acid, even though the acidified solution was allowed to stand for days. It was allowed to stand because it requires time for a complete precipitation of benzoic sulphinide from the solutions of its salts; and it was found, further, that adding concentrated hydrochloric acid to the extent of one-third the volume of the solution gave the quickest and most complete precipitation of benzoic sulphinide when this was formed, as in the experiments with stronger ammonia. The effect of the low temperature was only to retard the reaction and this was not marked. The following equation expresses the reaction:

$$C_7H_4SO_3Cl_2 + 4NH_3 = C_6H_4\begin{cases}CN\\SO_3NH_4\end{cases} + 2NH_4Cl.$$

Action of Strong Ammonia (1 : 3).—In carrying out the experiments with ammonia of this strength (1 volume saturated to 3 volumes water) at 0°, both the ethereal solution of the chloride and the ammonia solution were cooled to the temperature of melting ice and the ammonia added slowly, with constant stirring, to the chloride immersed in an ice-bath, where it remained until all the chloride was dissolved in the ammoniacal solution. In other experiments sometimes ethereal solutions and sometimes the dry chloride were used, and the temperature rose considerably during the reaction. The principal product was the same with this dilution of ammonia

as in all other cases, but here a considerable amount of the chloride was changed to the ammonium salt of benzoic sulphinide. The following table gives the amounts of benzoic sulphinide formed in several experiments:

Temperature.	Amount of chloride taken. Grams.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed to sulphinide.
0°	0.7492	0.1169	20.3
0°	0.5998	0.0842	18.2
0°	2.1112	0.1377	8.5
"	1.3978	0.0519	4.1
"	1.4362	0.0514	4.6
"	2.4384	0.2649	14.1
"	1.9301 (dry)	0.2191	14.8

The method used to precipitate the sulphinide is not strictly quantitative, but an effort was made to keep the conditions the same and thus make the results comparable. The filtrates did not taste sweet. I am unable to give any reason for the great variations.

Action of Concentrated Ammonia.—In a number of experiments the ordinary concentrated and saturated solutions of ammonia were used, and the products were the same as with the 1 : 3 solution. The reaction was very vigorous, and with the saturated solution it was explosive. In only one experiment was an effort made to influence the temperature of the reaction and in this the chloride and ammonia solutions were heated quickly in a water-bath at 80° C. The benzoic sulphinide obtained from three experiments was weighed and the yield was as follows:

Amount of chloride taken. Grams.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed to sulphinide.
1.2799 (dry)	0.1564	15.9
1.0873 (eth. sol.)	0.1388	16.6
0.5825 "	0.0737	16.4

This agrees fairly well with several results of the action of 1 : 3 ammonia.

Action of Water-free Ammonia.—The ammonia was passed through two drying cylinders filled with soda-lime and allowed to act upon the unsymmetrical chloride—either dry or

in solution in anhydrous ether or chloroform. When the chloride was dry it had to be broken up with a rod as fast as acted upon, because of a hard coating which protected the enclosed chloride. The heat of reaction was marked in all cases. In one experiment with 0.5 gram dissolved in about 40 cc. of ether the temperature at the beginning of the reaction was 20°; during the first half minute of the rapid passing of the gas it fell to 19°, and as soon as the products, which are insoluble in ether, began to form, the temperature rose rapidly to 28°—during a minute or two—and then fell to 14° at the end of thirty minutes. The room temperature was about 20°. In all the experiments with the unsymmetrical chloride, a very small quantity resisted the action of ammonia, and it was to insure the conversion of this that the gas was passed for so long a time. Experiments were carried out with dilute ethereal solutions cooled to 0° in an ice-bath, the solution being rapidly stirred while a slow current of gas was conducted into it, with the temperature held at 18°.5—that of a hydrant water-bath—and also upon the dry chloride and upon concentrated and dilute ethereal solutions, with no attempt to regulate the temperature. In no case could we obtain any product but ammonium cyanbenzenesulphonate. It did not even taste of benzoic sulphinide. As a check upon our test for other substances than the cyan salt, the amount of that substance was determined, as near as is possible with a substance so hard to separate from its by-products. The method used by List and Stein[1] was found to be the most satisfactory.

2.5519 grams of the chloride were dissolved in anhydrous ether and dry ammonia gas passed through the solution until the reaction was certainly complete. The ether was allowed to evaporate spontaneously, and a water solution of the residue was heated to 60° and treated with freshly precipitated silver oxide until there was no further precipitation of silver chloride. The filtered solution was then treated with freshly prepared ammonium sulphide until no more silver sulphide came down, and the resulting solution was evaporated

[1] Ber. d. chem. Ges., 31, 1649.

to dryness on a water-bath, dried by standing over sulphuric acid, and weighed. The weight was somewhat more than that called for by a quantitative conversion of the chloride into ammonium *o*-cyanbenzenesulphonate. This, together with the failure to find any other product, was considered conclusive evidence that the whole reaction is to be expressed by the equation

$$C_7H_4SO_2Cl_2 + 4NH_3 = C_6H_4\begin{cases}CN\\SO_2NH_4\end{cases} + 2NH_4Cl.$$

Experiments with Benzoic Sulphinide.—To see how far the conditions of the experiments with the unsymmetrical chloride affected the salt of benzoic sulphinide that might be formed in the reaction, pure benzoic sulphinide was subjected to the same treatment, with these results :

Sulphinide taken. Grams.	Sulphinide recovered. Grams.	Loss. Per cent.
1.8564	1.8064	2.7
1.9481	1.9067	2.1

The results of a third experiment may as well be recorded, although the conditions tending to hydrolysis were in no wise comparable to those under which ammonia acted upon the chloride : 1.3375 grams of pure benzoic sulphinide were dissolved in boiling hot water and one-third of its volume of concentrated hydrochloric acid immediately added. After standing several hours the precipitate was filtered, dried, and weighed. It showed a loss of 8.4 per cent.

Action of Ammonia on the Symmetrical Chloride—The action of dry and aqueous ammonia upon the symmetrical chloride was also studied where experiments parallel to those with the unsymmetrical seemed desirable, and the results were in entire accordance with those of work previously done in this laboratory. The speed of reaction as compared with that of the unsymmetrical was very slow. The results of the only experiments in which the amount of benzoic sulphinide precipitated by hydrochloric acid was determined are as follows :

Strength of ammonia.	Amount of chloride taken. Gram.	Amount of sulphinide obtained. Gram.	Per cent of chloride changed.
1 : 3	0.3535 (dry)	0.2551	93.7
Saturated	0.8613 (ether)	0.5679	85.6
Dry	0.7439 "	0.5027	87.8

The amount of sulphinide, which cannot be recovered by this method, represented, of course, a large percentage of the small quantity of chloride used in the above experiments, and hence the variation from the theoretical does not necessarily signify that anything else was formed. It is not unlikely that the same cause of variation operated here as in the case of the unsymmetrical chloride and 1 : 3 ammonia. It was impossible to detect any other substance than the ammonium salt of benzoic sulphinide and ammonium chloride in the product.

Ammonium o-Cyanbenzenesulphonate and Ammonium o-Carbaminebenzenesulphonate.—For the sake of completeness the properties of ammonium *o*-cyanbenzenesulphonate are given here, although it has been fully described by those who have obtained it previously. It crystallizes from alcoholic solutions in white botryoidal masses of needles. The second form of crystals, rosettes of transparent needles, described by Karslake, was not obtained.[1] It is very soluble in water and hot alcohol, moderately soluble in cold alcohol, and insoluble in dry ether. I found it easier to hydrolyze it to *o*-sulphobenzoic acid than my interpretation of most remarks on this subject led me to think. The hydrolysis was effected by boiling for ten hours a solution acidified with hydrochloric acid. In how short a time this transformation can be effected was not determined. The passage from the substance of the formula $C_6H_4\begin{cases}CN\\SO_2NH_4\end{cases}$ to one of the formula $C_6H_4\begin{cases}CONH_2\\SO_2NH_4\end{cases}$ was repeatedly accomplished by simply evaporating to dryness on a water-bath the solutions from which benzoic sulphinide had been precipitated by hydrochloric acid. Water alone does not hydrolyze it.

The ammonium carbaminebenzenesulphonate, obtained

[1] This JOURNAL, 18, 820.

from the cyan salt, crystallized out in two forms, white needles and large, thick crystals (the long axis of one was nearly a centimeter in length), behaving exactly like the ammonium cyanbenzenesulphonate described by Karslake, and like his substance also, the thick crystals recrystallized as needles.[1] In every instance in which the melting-point of the carbamine salt was taken the first crystals melted gradually from 250° to 260°, and when recrystallized they melted at 256° to 257°.[2]

Much difficulty was experienced in getting ammonium *o*-cyanbenzenesulphonate free from the last traces of ammonium chloride, yet it was accomplished by repeatedly recrystallizing it from absolute alcohol. But the potassium salt can be obtained without difficulty. It is only necessary to add a saturated solution of potassium carbonate to a solution containing the products formed by the action of ammonia on the chloride even if it is moderately dilute, when a fine, white, crystalline powder is precipitated. The potassium salt crystallizes easily from a water solution in beautiful, thick, square-ended, transparent needles, radiating from centers. This was also found to be a ready method of following the process of hydrolysis, as the potassium salt of orthocarbaminesulphonic acid only crystallizes from very concentrated water solutions and is not precipitated by potassium carbonate, while, as has been said, the potassium cyan salt can be obtained from quite dilute solutions by rubbing the sides of the beaker.

Action of Alcohols and Alcoholates.

Earlier work of Remsen and Dohme,[3] Karslake,[4] and List

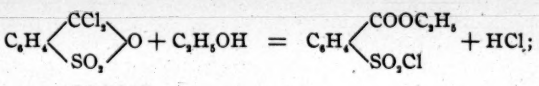
[1] This JOURNAL, 18, 831.

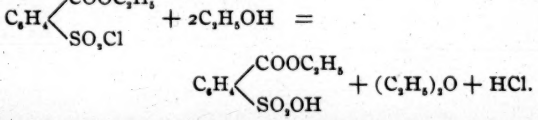
[2] Karslake gave 219° to 220° as the melting-point of the substance he obtained on heating an acidified solution of the cyan salt (*Ibid.*, 18, 825). Fahlberg and Barge described a salt which they proved to be ammonium orthocyanbenzenesulphonate as thin, transparent needles, melting at 255° to 256° (Ber. d. chem. Ges., 22, 759). F. D. Wilson described it as large plates melting at 262° to 263° (Dissertation, J. H. U., 1899, p. 26). M. D. Sohon described it as needles melting at 256° to 257° (This JOURNAL, 20, 269). Karslake's substance did not lose weight when heated, but all the others described it as losing water of crystallization when heated to 125° C. The salt which I obtained agreed with the latter.

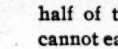
[3] This JOURNAL, 11, 341.

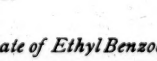
[4] *Ibid.*, 18, 825.

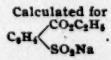
and Stein[1] has shown that the two chlorides react with alcohol first to form ester chlorides which by further action of the alcohols pass over into the corresponding ester acids:





The ester chloride is easily formed from the unsymmetrical chloride; less easily from the symmetrical chloride. When, however, the symmetrical chloride is dissolved in anhydrous ether and a slightly warm emulsion of sodium ethylate (2 mols. ethylate to 1 mol. chloride) in absolute alcohol added to the solution, reaction takes place smoothly until about one-half of the alcoholate has been added, when it stops and cannot easily be carried farther. An oil was obtained from the solution that had the general properties of the ester chloride,  , though the evidence that it is this substance is not conclusive.

Sodium Orthosulphonate of Ethyl Benzoate,  .—This was obtained by dissolving the symmetrical chloride in ethyl alcohol and treating it with an alcoholic emulsion of sodium ethylate and allowing it to stand for two or three hours. The solution became slightly warm. After heating the purified salt to constant weight it was analyzed:

	Calculated for 	Found.
Na	9.12	9.38

[1] Ber. d. chem. Ges., 31, 1659.

The same compound was obtained by treating dry sodium ethylate with an excess of the *o*-sulphone chloride of ethyl benzoate made from the unsymmetrical chloride, and extracting the product with ethyl alcohol. After drying to constant weight the salt gave:

	Calculated for $C_6H_4(CO_2C_2H_5)(SO_3Na)$.	Found.
Na	9.12	9.20

It crystallizes in beautiful, transparent, colorless leaves and elongated hexagons with beveled edges.

Silver Orthosulphonate of Methyl Benzoate, $C_6H_4(CO_2CH_3)(SO_3Ag)$. —

On analysis this salt gave the following figures:

	Calculated for $C_6H_4(CO_2CH_3)(SO_3Ag)$.	Found. I.	Found. II.
Ag	33.41	33.76	33.10

Barium Orthosulphonate of Methyl Benzoate, $\left(C_6H_4(CO_2CH_3)(SO_2O)\right)_2Ba$.—Analysis gave:

	Air-dried crystals. Calculated for $\left(C_6H_4(CO_2CH_3)(SO_2O)\right)_2Ba+H_2O$.	Found.	After heating to constant weight. Calculated for $\left(C_6H_4(CO_2CH_3)(SO_2O)\right)_2Ba$.	Found.
Ba	23.46	23.63	24.20	24.40

Sodium Orthosulphonate of Methyl Benzoate, $C_6H_4(CO_2CH_3)(SO_3Na)$.

—Dry unsymmetrical chloride was added gradually to a saturated methyl alcoholic solution of sodium methylate and the gelatinous product filtered with suction through a platinum cone. It was evaporated by a current of dry air and recrystallized from methyl alcohol and from water several times. At first it crystallized in long, transparent, colorless needles, but on standing a few hours they changed completely to cubes

and irregular crystals, looking as if the needles had been broken up. No other product was discovered. It was analyzed for sodium, carbon, hydrogen, and water of crystallization.

	Calculated for $C_6H_4\langle^{CO_2CH_3}_{SO_3Na} + 2.H_2O$.	Found.
Na	8.40	8.47
C (mean)	35.00	35.03
H "	4.00	3.80
H_2O	13.10	12.73

It is thus seen that the acid of the formula $C_6H_4\langle^{CO_2C_2H_5}_{SO_3OH}$ was obtained from the symmetrical chloride and sodium ethylate, and from the chloride $C_6H_4\langle^{CO_2C_2H_5}_{SO_2Cl}$, formed from the unsymmetrical chloride. The corresponding methyl ester of the formula $C_6H_4\langle^{CO_2CH_3}_{SO_3OH}$ was obtained from both chlorides and boiling methyl alcohol, and from the unsymmetrical chloride and sodium methylate.

Neutral Sodium Salt of o-Sulphobenzoic Acid, $C_6H_4\langle^{CO_2Na}_{SO_3Na}$.—The dry crystals of the *o*-sulphone chloride of methyl benzoate were treated with a saturated methyl alcoholic solution of sodium methylate in small excess. The reaction was so vigorous that the alcohol boiled. The solution was filtered, extracted with ether and methyl alcohol, and the residue dissolved in water. Out of this came beautiful rosettes of transparent, colorless needles, which, when analyzed for sodium, gave:

	Calculated for $C_6H_4\langle^{CO_2Na}_{SO_3Na}$.	Found.
Na	18.80	19.22

Unidentified Products.

(*a*) Small quantities of dry unsymmetrical chloride and dry

sodium ethylate (in the proportion of 1 molecule of the former to 2 of the latter) were mixed and ground fine in a mortar, the intention being to dissolve the mixture and eliminate as far as possible any action due to an excess of one or the other. Something called me off for perhaps ten minutes, and when I again touched the mixture with the pestle an explosion took place which resembled that of powder in an open vessel. Dense, white fumes with a peculiar and suffocating odor were given off, and a dry, light-brown mass remained, resembling crushed lava. The mortar was made hot through and through. The material was extracted with anhydrous ether and nothing obtained. Extraction with anhydrous alcohol yielded a little oil. Very concentrated ammonia was added to this oil and the excess of ammonia boiled off, but the solution did not become sweet. It was boiled with water, and on adding silver nitrate a white precipitate was formed, but this dissolved on boiling and did not coagulate, hence it was not silver chloride. There was not enough for further study. After extracting with alcohol, the residue dissolved in water, forming a neutral, amber-colored solution which, when evaporated in a desiccator, yielded dirty-looking crystals, which were apparently nothing but impure sodium chloride.

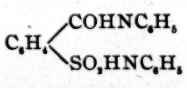
(*b*) A saturated solution of sodium methylate in methyl alcohol was added to dry, unsymmetrical chloride. The reaction was explosive. By immersing in hot water and passing a rapid current of dry air over it, the solution was evaporated to dryness and then extracted with dry ether. On evaporating off the ether an oil appeared which soon solidified. This was dissolved in methyl alcohol and evaporated down. It strongly resisted crystallizing, but on putting it in a freezing-mixture it came down quickly in diamond-shaped crystals, which melted at 38° to 39°. This was recrystallized three times without change in the melting-point, and the final product was well washed with water. Heating for two hours at 50° to 55° caused it to lose 1.01 per cent in weight. When absorbed in water the distillate gave the reaction for methyl alcohol. It is insoluble in cold water, but readily soluble in hot water, alcohol, and ether. When boiled with water it

showed no acid properties, but when silver nitrate was added silver chloride was precipitated. After boiling with dilute aqueous ammonia the solution had a faintly sweet taste. On treating an ethereal solution with dry ammonia, ammonium chloride was precipitated, and from the ethereal solution some crystals were obtained, which melted gradually from 38° to 85°, apparently in two stages. They were slightly soluble in cold water, but easily soluble in hot water, ether, and alcohol. On attempting to recrystallize them the first time, a small quantity did not pass into solution, and this was found to melt at 132° to 135°. The ethereal solution of the rest was again treated, for thirty minutes, with ammonia gas, and after evaporation an oil remained and a few crystals like those above. The oil solidified in a freezing-mixture but again melted at the room temperature. I was unable to get a pure product out of the little that I had to work with.

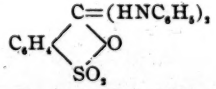
II. ACTION OF ANILINE UPON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

By W. B. Holmes.

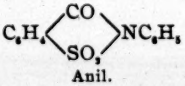
The action of aniline on these chlorides has been the subject of numerous investigations in this laboratory. Three products have been isolated, a symmetrical anilide, an unsymmetrical anilide, and an anil. These have been clearly shown to have the following formulas:



Symmetrical anilide.



Unsymmetrical anilide.



Anil.

It was found that when aniline was added to an emulsion of the symmetrical chloride in a large amount of cold water and the reaction allowed to proceed slowly, only the symmetrical anilide and the anil were formed. With the unsymmetrical

chloride, under similar conditions, only the two anilides were obtained, but a much larger percentage of the unsymmetrical anilide. These facts form one of the chief arguments for the assignment of the symmetrical and unsymmetrical formulas to the chlorides melting at 79° and 40°, respectively.

List and Stein[1] have recently tried the action of aniline on these chlorides. They brought the chloride and aniline together in a cold ethereal solution and obtained from each chloride all three products. They therefore claimed that the action of aniline on the chlorides affords no good grounds for assigning the symmetrical or unsymmetrical structure to either chloride. In view of their criticism a careful study of the action of aniline on each chloride was made under different conditions.

The relative amounts of the products formed depends largely upon the method employed for bringing the aniline and chloride together. The temperature at which the reaction takes place has a large influence upon the results. Either chloride, when heated with aniline alone, gives a mixture of all three products, the reaction being very violent in the case of the unsymmetrical chloride. When the symmetrical chloride is dissolved in anhydrous ether or chloroform, and aniline added, no reaction takes place. If this solution is heated on a water-bath, reaction takes place only when the ether or chloroform has been driven off. This is equivalent to heating the chloride and aniline together and then all three products are obtained. When the unsymmetrical chloride is dissolved in anhydrous ether or chloroform and aniline added, reaction takes place at once and all three products are obtained.

The best method is to add the aniline to an emulsion of the chloride in a large amount of cold water. Reaction takes place slowly without the evolution of heat. With the symmetrical chloride only the symmetrical anilide and anil are obtained, while with the unsymmetrical chloride both anilides are obtained but with a much larger percentage of the unsymmetrical anilide. The following results confirm the previous work done in this laboratory.

[1] Ber. d. chem. Ges., 31, 1648.

Action of Aniline upon the Symmetrical Chloride.—Three grams finely powdered chloride were placed in an Erlenmeyer flask with about 150 cc. of water. Aniline, in the proportion of 4 molecules of aniline to 1 of the chloride was then added and the contents of the flask vigorously shaken. At first there was no apparent reaction, the chloride simply dissolving in the aniline. After the lapse of three or four hours the aniline solution gradually solidified. The solid mass was then broken up and more aniline added. The resulting viscous mass was allowed to stand for two days with occasional shaking. The temperature of the water throughout the experiment varied little from 14°.

Hydrochloric acid was then added, the contents of the flask transferred to a mortar, and thoroughly ground up to remove the excess of aniline. The filtrate was evaporated and examined for the unsymmetrical anilide. If present, this substance would appear in the filtrate, as it is sparingly soluble in water and is not decomposed by hydrochloric acid. No trace of the unsymmetrical anilide could be obtained from the filtrates in a large number of experiments.

The residue was then treated with a dilute solution of sodium hydroxide. The undissolved precipitate consisted only of the anil. When the filtrate was acidified with hydrochloric acid only the symmetrical anilide was precipitated. From this precipitate and filtrate no trace of the unsymmetrical anilide could be obtained. The products of the reaction were only the anil and the symmetrical anilide. The chloride unaccounted for in the results was hydrolyzed to orthosulphobenzoic acid.

	Chloride used. Grams.	Total product. Grams.	Anil. Grams.	Symmetrical anilide. Grams.
1	3	3.19	1.96	1.23
2	3	3.15	1.80	1.35
3	3	3.20	1.94	1.26
4	3	3.24	1.98	1.26
5	3	3.36	2.01	1.35

	Chloride converted to anil. Grams.	Chloride converted to symmetrical anilide. Gram.	Chloride not accounted for. Gram.
1	1.81	0.84	0.30
2	1.66	0.91	0.43
3	1.79	0.85	0.36
4	1.83	0.85	0.32
5	1.85	0.91	0.24

Action of Aniline upon the Unsymmetrical Chloride.—The same method of procedure was employed in these experiments, except that the flasks were kept in ice-water for several hours after the experiment had started. Reaction took place much more quickly than with the symmetrical chloride. The aniline solution became solid in a very short time. The solid mass was then broken up and more aniline added. The viscous mass was allowed to stand for two days with occasional shaking. Hydrochloric acid was then added, the contents transferred to a mortar and thoroughly ground up to remove the excess of aniline. From the filtrate, part of the unsymmetrical anilide was obtained. The precipitate dissolved completely in a dilute solution of sodium hydroxide, showing that there was no anil formed. Hydrochloric acid precipitated a mixture of the anilides. The precipitate was washed with a large amount of water to remove the unsymmetrical anilide. When a constant weight had been obtained the product, when crystallized from alcohol, gave only the symmetrical anilide. The products of the reaction were only the symmetrical and unsymmetrical anilides, but with a much larger percentage of the unsymmetrical product. The chloride unaccounted for in the following results was probably hydrolyzed to orthosulphobenzoic acid.

	Chloride used. Grams.	Total product. Grams.	Symmetrical anilide. Grams.	Unsymmetrical anilide. Grams.
1	3	3.81	1.56	2.25
2	3	3.70	1.42	2.28
3	3	3.75	1.45	2.30
4	3	3.78	1.49	2.29
5	3	3.86	1.55	2.31

	Chloride converted to unsymmetrical anilide. Grams.	Chloride converted to unsymmetrical anilide. Grams.	Chloride not accounted for. Gram.
1	1.05	1.53	0.42
2	0.96	1.55	0.49
3	0.98	1.56	0.46
4	1.01	1.56	0.43
5	1.05	1.58	0.37

III. THE ACTION OF ALIPHATIC AMINES ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

By Friend E. Clark.

The action of ammonia and of aromatic amines upon the chlorides of orthosulphobenzoic acid has been studied in this laboratory, but the action of the aliphatic amines has not yet been investigated. In view of the remarkable relationship between the two chlorides, the study of their conduct under a variety of conditions is important. This investigation has to deal with their conduct towards methylamine, ethylamine, and dimethylamine.

The methyl- and dimethylamines were obtained from the corresponding hydrochlorides by treating their concentrated solutions with solid potassium hydroxide. In most of the experiments the employment of the dry amines was necessary. The drying of the gases was accomplished by passing them through one or more Peligot tubes, filled with pulverized sodium or potassium hydroxide. In cases where the anhydrous gas was not needed, the amine was passed directly into a vessel containing the chloride, or into water and afterwards used in the form of the aqueous solution.

Ethylamine was obtained from Kahlbaum, Berlin, in anhydrous condition, sealed in stout glass vessels. As the liquid amine was needed only in a few experiments, it was kept in the form of a 20 per cent aqueous solution, from which the free base was liberated as desired by adding solid potash.

Action of Methylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—Substituted ammonias of the aromatic

[1] From the dissertation of the author, submitted June, 1902, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

series yield two classes of compounds according to the conditions of the reactions. Aniline, for example, gives the dianilide and the anil. Methylamine and the symmetrical chloride, on the other hand, form one compound only, namely, the methyl ester of benzoic sulphinide, which corresponds to the anil obtained with aniline.

Dry methylamine was conducted into a solution of the symmetrical chloride in anhydrous ether. Immediately there appeared a white precipitate, that in every instance in which the temperature of the solution was kept below 25° C. and the flow of amine properly regulated, had a crystalline structure. Considerable difficulty was experienced in securing the proper conditions for the successful performance of the experiment. For example, even though the temperature of the solution of the chloride was lowered to 10° C., the temperature would rise very rapidly and the product be gummy, if the amine was allowed to pass into it rapidly. Methylamine hydrochloride, which was always one of the products of the reaction, was almost wholly precipitated from the solution, carrying down varying amounts of the ester with it. It was expedient to allow the ether to evaporate at ordinary laboratory temperatures. The mixture, which, under most favorable conditions, consisted of a white, flocculent mass, was transferred to a funnel and washed a few times with cold water in order to remove the methylamine hydrochloride. The residue was crystallized from alcohol and analyzed, and found to be the methyl ester of benzoic sulphinide. The reaction between the amine and symmetrical chloride can be represented by the equation :

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + 3NH_2CH_3 = C_6H_4\begin{cases}CO\\SO_2\end{cases}N.CH_3 + 2NH_2CH_3.HCl.$$

0.2121 gram substance gave 0.2595 gram $BaSO_4$.
0.1149 gram substance gave 0.1394 gram $BaSO_4$.
0.0928 gram substance gave 0.1131 gram $BaSO_4$.

0.1354 gram substance gave 0.0083 gram N.
0.1312 gram substance gave 0.2326 gram CO_2.
0.1312 gram substance gave 0.0439 gram H_2O.

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle N.CH_3$.	Found. I.	II.	III.	IV.	V.
C	48.68	....	....	....	....	48.34
H	3.53	....	....	....	....	3.24
N	7.07	....	....	....	6.13	....
S	16.26	16.89	16.65	16.73	....	....

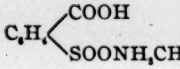
The sulphur had to be determined by the method of Liebig. Many attempts were made to oxidize the ester with fuming nitric acid, according to the method of Carius, at temperatures as high as 350° C. Almost invariably a portion of the substance would resist the action of the acid. The nitrogen was determined by the Kjeldahl method.

Methyl benzoic sulphinide is slightly soluble in hot water, melting to a colorless oil, and practically insoluble in cold water. It is quite soluble in ether, more sparingly in absolute alcohol. From ethyl alcohol it crystallizes in fine needles; from a mixture of alcohol and water (about a 60 per cent solution) in large prisms terminating in pyramidal faces. The ester can be most easily obtained in pure crystalline condition by dissolving it in hot alcohol and adding warm water until the solution becomes cloudy, then heating on a water-bath until complete solution ensues, and allowing it to cool slowly. It is not sweet. It melts at 129° C.

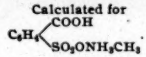
Methyl benzoic sulphinide has been previously obtained by Remsen and Palmer[1] by heating the silver salt of the sulphinide with methyl iodide. Its melting-point is given by them as 128° to 129°.

Behavior of Methyl Benzoic Sulphinide in the Presence of Acids and Alkalies.—When boiled with the ester for twelve or fourteen hours, aqueous hydrochloric acid hydrolyzed it, forming the acid methylammonium salt of orthosulphobenzoic acid, which crystallized in radiating needles. One determination of sulphur indicated a compound of the formula

[1] This JOURNAL, 8, 226.

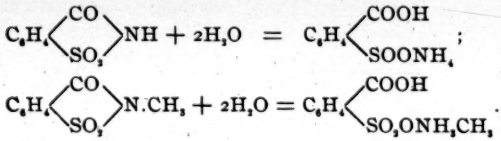


0.2145 gram substance gave 0.2152 gram $BaSO_4$.

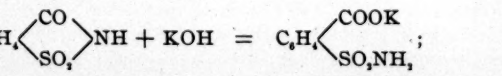
	Calculated for 	Found.
S	13.74	13.79

When the acid methylammonium salt is heated with potassium hydroxide, neutral potassium orthosulphobenzoate and methylamine are formed. The acid potassium salt of orthosulphobenzoic acid is precipitated on the addition of hydrochloric acid to the aqueous solution of the neutral potassium salt.

The formation of the acid methylammonium salt of orthosulphobenzoic acid is in every way analogous to the action of hydrochloric acid on benzoic sulphinide:



Just as benzoic sulphinide is converted into orthosulphaminebenzoic acid by treating it with dilute potassium hydroxide, so the methyl ester is hydrolyzed to orthomethylsulphaminebenzoic acid:



One essential difference is to be noted, however. Aqueous alkalies do not effect the transformation in the latter case, alcoholic alkalies being necessary, and even then five or six hours' heating is required for the complete hydrolysis. It is of interest to note also that the alkali metals form the di-

metallic salts, while the metals of the alkaline earths replace only the hydrogen of the carboxyl group.

Potassium orthomethylsulphaminebenzoate crystallizes from alcohol in small plates. It is extremely soluble in water and alcohol, insoluble in petroleum ether.

0.1875 gram substance gave 0.1121 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{COOK}_{SO_2NKCH_3}$	Found.
K	26.27	26.35

Barium hydroxide and the methyl ester give the barium salt of orthomethylsulphaminebenzoic acid. It is so soluble in water and alcohol that no crystals of it were obtained. From a mixture of benzene and ligroin an amorphous powder was obtained, from which two determinations of barium were made.

0.3014 gram substance gave 0.1281 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\langle^{COO}_{SO_2NHCH_3}\right)$Ba.	Found.
Ba	24.29	25.01

Preparation of Orthomethylsulphaminebenzoic Acid from Orthotoluenesulphone Methylamide. — Orthotoluenesulphone chloride was treated with a strong aqueous solution of methylamine. In the presence of a large excess of the amine, the toluenesulphone methylamide remains in semi-solid condition, so that one is quite easily misled in regard to the end of the reaction. The solution was cooled with ice-water and the amide separated by filtration. Orthotoluenesulphone methylamide was found to be insoluble in cold water, slightly insoluble in hot water, quite soluble in absolute alcohol, but from the last it did not crystallize in good condition. It is furthermore soluble in acetone and chloroform, thin, striated plates crystallizing from the former (m. p. 73° to 75° C.). The methylamide was found to be quite insoluble in cold benzene and almost insoluble in cold ligroin. A mixture of the two solvents gave the best results.

If the proper amount of ligroin is added to a solution of the

amide in benzene, the amide comes out in the form of beautiful, colorless needles after one crystallization. Slow crystallization gives plates; rapid crystallization gives needles. The melting-point of both products is 74° to 75° C.

I. 0.1969 gram substance gave, by Liebig's method, 0.2510 gram $BaSO_4$.

II. 0.2033 gram substance gave, by Liebig's method, 0.2550 gram $BaSO_4$.

III. 0.1956 gram substance gave 0.3739 gram CO_2 and 0.1038 gram H_2O.

IV. 0.2216 gram substance gave 0.4186 gram CO_2 and 0.1191 gram H_2O.

	Calculated for $C_6H_4\langle^{CH_3}_{SO_2NHCH_3}$.	Found. I.	II.	III.	IV.
S	17.31	17.45	16.92	....	....
C	51.77	....	....	52.12	51.51
H	6.06	....	....	5.94	6.01

The oxidation of the amide with potassium permanganate in alkaline solution gave rise to the formation of a small amount of the potassium salt of orthomethylsulphaminebenzoic acid, which, when acidified with hydrochloric acid at the ordinary temperature, passed to the methyl ester of benzoic sulphinide. However, when the temperature of the solution was lowered to about 10° C., the acid added cautiously, and the resulting solution allowed to evaporate slowly, orthomethylsulphaminebenzoic acid crystallized from the solution in small, radiating needles. The acid has no constant melting-point. It begins to soften at 70° C. and is not completely reduced to a clear liquid below 126° C. If the temperature is kept at the latter point for some minutes, then allowed to fall slowly, the product remaining in the tube will melt at 127° to 129° C., which indicates the formation of methyl benzoic sulphinide from orthomethylsulphaminebenzoic acid by the loss of 1 molecule of water.

Action of Aqueous Methylamine on the Symmetrical Chloride.—When a 20 per cent solution of methylamine in water is added to the pure symmetrical chloride of orthosulphobenzoic

acid, reaction begins at the ordinary temperature, with the formation of methyl benzoic sulphinide and methylamine hydrochloride. At low temperatures a second compound is formed. This crystallizes in needles (m. p. 74° C.) and is probably the symmetrical dimethylamide of orthosulphobenzoic acid, $C_6H_4\begin{cases}CONHCH_3\\SO_2NHCH_3\end{cases}$, analogous to the symmetrical dianilide, $C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases}$, which has been fully described by other investigators. The product melting at 74° C. was obtained in insufficient quantities for analysis.

Action of Methylamine on the Unsymmetrical Chloride.— When the dry amine was passed rapidly into the solution of the unsymmetrical chloride in anhydrous ether, the temperature was soon raised to the melting-point of the chloride and the boiling-point of the ether. The ether, saturated with the methylamine vapors, carried over small quantities of the chloride, which, in contact with the air, presented a white, cloud-like appearance.

The products were treated differently, according to circumstances. When the products were viscous, the mixture was dissolved in anhydrous alcohol and attempts made to separate them by fractional crystallization. These attempts were not entirely successful, as will be shown later. However, when the reaction continued smoothly and the hydrochloride precipitated in dry, flaky condition, the entire product, after the evaporation of the ether at the ordinary laboratory temperature, was washed with ice-water in order to remove the methylamine hydrochloride. The residue is quickly pressed between layers of filter-paper and thoroughly dried. At least two compounds are formed when methylamine acts on the unsymmetrical chloride. On dissolving the dry product in warm anhydrous alcohol the methyl ester of benzoic sulphinide crystallizes out of the cold solution. The ester was also formed and in somewhat larger quantities, when the product was dissolved in dilute alcohol. The methyl benzoic

sulphinide was found to be identical with that obtained from the symmetrical chloride and methylamine. The second compound of the reaction proved to be the unsymmetrical dimethylamide of orthosulphobenzoic acid.

At times as much as 15 per cent of methyl benzoic sulphinide is formed. This invariably crystallizes first, and can be separated from the syrupy mass by means of a Witt plate and a filter-pump. The unsymmetrical derivative rarely crystallized from the remaining syrup. On the other hand, it was obtained more frequently when the product from the methylamine and unsymmetrical chloride was dissolved in an excess of anhydrous ethyl alcohol at ordinary temperatures, and the solvent evaporated by passing a current of dry air over the solution, or by allowing the solution to remain in a sulphuric acid desiccator until crystallization was complete.

Infusible Dimethylamide of Orthosulphobenzoic Acid, $C_6H_4\begin{cases}C=(NHCH_3)_2\\ \\ SO_2\end{cases}O$, is obtained by the action of methylamine on the unsymmetrical chloride at low temperatures. It crystallizes from alcohol in plates, which are insoluble in cold water. In fact the best method of obtaining the crystals free from the mother-liquor is to wash them thoroughly with water. The amide does not fuse at 330° C. Above this temperature decomposition begins. The following analytical results were obtained for carbon and hydrogen.

0.2531 gram substance gave 0.4418 gram CO_2 and 0.1231 gram H_2O.

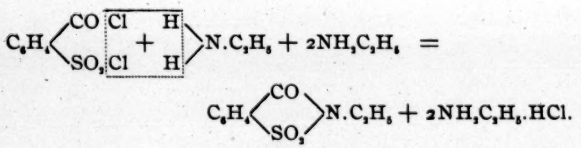
	Calculated for $C_6H_4\begin{cases}C=(NHCH_3)_2\\ \\ SO_2\end{cases}O$	Found.
C	47.75	47.60
H	5.35	5.46

Evidently this compound is isomeric with the amide of the formula $C_6H_4\begin{cases}CO.NHCH_3\\ \\ SO_2NHCH_3\end{cases}$, but, as has been stated, such a

compound has not been obtained except possibly in very small quantity.

It should be said that the products obtained from the action of methylamine on the unsymmetrical chloride are not easily obtained. By far the largest part of the product does not crystallize and could not be further investigated.

Action of Ethylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—Ethyl benzoic sulphinide is the sole product of the action of anhydrous ethylamine on the symmetrical chloride in dry ethereal solution :



The compound was isolated by extracting the ethylamine hydrochloride from the white, pulverulent residue obtained from the ether solution with cold water and crystallizing the ethyl derivative from alcohol. It is soluble in ethyl alcohol, less so in methyl alcohol, quite soluble in acetone and benzene, slightly soluble in ligroin and warm water, and practically insoluble in cold water. Ethyl benzoic sulphinide crystallizes from dilute ethyl alcohol in acicular crystals and from anhydrous alcohol in stout prisms, melting at 94° C.

This compound has been obtained by Fahlberg and List[1] by treating sodium benzoic sulphinide with ethyl iodide at 230°, and by Brackett[2] by treating the silver salt of benzoic sulphinide with ethyl iodide. It was analyzed with the following results :

I. 0.0417 gram substance gave, by Liebig's method, 0.0503 gram $BaSO_4$.

II. 0.0964 gram substance gave, by Liebig's method, 0.1171 gram $BaSO_4$.

III. 0.1737 gram substance gave, by Liebig's method, 0.2045 gram $BaSO_4$.

[1] Ber. d. chem. Ges., 20, 1598.

[2] This JOURNAL, 9, 496.

IV. 0.2158 gram substance gave 0.4062 gram CO_2 and 0.0812 gram H_2O.

V. 0.3012 gram substance gave 0.6415 gram CO_2 and 0.1106 gram H_2O.

VI. 0.1975 gram substance gave, by the Kjeldahl method, 0.0156 gram NH_3.

VII. 0.2004 gram substance gave, by the Kjeldahl method, 0.0163 gram NH_3.

	Calculated for $C_6H_4\langle^{CO}_{SO_2}\rangle N.C_2H_5$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
S	16.28	16.57	16.77	16.18	....	....	....	....
C	51.31	....	....	....	51.34	51.29	....	....
H	4.25	....	....	....	4.19	4.14	....	....
N	6.63	....	....	....	....	....	6.59	6.67

Orthoethylsulphaminebenzoic Acid.—Ethyl benzoic sulphinide passes to orthoethylsulphaminebenzoic acid when hydrolyzed with alcoholic alkalies:

$$C_6H_4\langle^{CO}_{SO_2}\rangle N.C_2H_5 + 2KOH = C_6H_4\langle^{COOK}_{SO_2NKC_2H_6} + H_2O.$$

The neutral potassium orthosulphaminebenzoate crystallizes from water in very small plates, which are extremely soluble in water. Two determinations of the water of crystallization indicated 2 molecules. The anhydrous salt, when heated with sulphuric acid, yielded the following results:

0.2005 gram substance gave 0.0992 gram K_2SO_4.

0.2851 gram substance gave 0.1415 gram K_2SO_4.

	Calculated for $C_6H_4\langle^{COOK}_{SO_2NKC_2H_6}$.	Found. I.	II.
K	22.11	22.21	22.31

By heating the ethyl ester in a retort connected with a reflux condenser, for six hours, with an alcoholic solution of barium hydroxide, barium orthoethylsulphaminebenzoate was formed.

0.5102 gram substance gave 0.2020 gram $BaSO_4$.

	Calculated for $\left(C_6H_4\begin{matrix}COO\\SO_2NHC_2H_5\end{matrix}\right)_2Ba$.	Found.
Ba	23.10	23.29

It is necessary to heat the ethyl ester for two days with dilute hydrochloric acid in order to transform it completely into the ethyl ammonium salt of orthosulphobenzoic acid.

The *ethyl ammonium salt* crystallizes from water in the form of delicate needles. One determination of sulphur was made.

0.2154 gram substance gave, by Liebig's method, 0.2053 gram $BaSO_4$.

	Calculated for $C_6H_4\begin{matrix}COOH\\SO_2ONH_3C_2H_5\end{matrix}$.	Found.
S	12.96	13.10

Action of Ethylamine on the Unsymmetrical Chloride.—Ethylamine, like methylamine, reacts in two ways at least with the unsymmetrical chloride. First, with the formation of the symmetrical derivative; secondly, with the formation of the infusible diethylamide of orthosulphobenzoic acid. When the product is heated with dilute alcohol, ethyl benzoic sulphinide is formed in somewhat larger quantity than in the case of methylamine and the unsymmetrical chloride. One crystallization only was necessary to bring the melting-point of the ethyl ester thus obtained to that of the product obtained from the symmetrical chloride (94° C.). There is no danger of mistaking the ester. It is perfectly characteristic in all of its reactions.

Although these reactions—of methyl- and ethylamines with the unsymmetrical chloride—are seemingly analogous in every way, there is a larger percentage of the ethyl ester formed. Experiments carried out under comparable conditions—temperature of the solutions, rate of flow of the amine, dilution of the alcohol, etc.—all confirm this statement. And, further, the ethyl ester can be removed from the reaction-products with less difficulty than in the case of the methyl ester.

The second of the products of the action of ethylamine on the unsymmetrical chloride was the infusible diethylamide of

orthosulphobenzoic acid. The infusible diethylamide was obtained by evaporating slowly the alcoholic solution of the products, from which the ethylamine hydrochloride had been removed. The largest and most satisfactory crystals were obtained from an alcoholic solution, that required more than two months for the evaporation of the solvent—about 150 cc.

The infusible diethylamide of orthosulphobenzoic acid crystallizes in beautiful, rhombic prisms, that are insoluble in petroleum ether and chloroform; sparingly soluble in benzene and acetone; reasonably soluble in methyl and ethyl alcohols, to a less degree in the former; and insoluble in water. It yielded the following results when analyzed:

0.2754 gram substance gave 0.4991 gram CO_2 and 0.1469 gram H_2O.

	Calculated for $C_6H_4\langle^{C=(NHC_2H_5)_2}_{SO_2}\rangle O$	Found.
C	49.53	49.41
H	6.56	5.98

At 0° C., or slightly above this temperature, the liquid amine reacts with the unsymmetrical chloride quite satisfactorily. The product, which was colored slightly yellow, was freed from the ethylamine hydrochloride by washing it with ice-cold water. The only compound that was certainly identified was the ethyl ester of benzoic sulphinide. At —20° C. anhydrous ethylamine is entirely without action on the unsymmetrical chloride of orthosulphobenzoic acid.

Action of Diethylamine on the Symmetrical Chloride of Orthosulphobenzoic Acid.—The symmetrical chloride is quantitatively transformed into the symmetrical tetramethyldiamide of orthosulphobenzoic acid by dimethylamine in solution in anhydrous ether, according to the following reaction:

$$C_6H_4\langle^{CO\,Cl}_{SO_2\,Cl}\rangle + \begin{matrix}H\,N(CH_3)_2\\ H\,N(CH_3)_2\end{matrix} + 2NH(CH_3)_2 =$$

$$C_6H_4\langle^{CO.N(CH_3)_2}_{SO_2N(CH_3)_2}\rangle + 2NH(CH_3)_2.HCl.$$

It crystallizes very well from an alcoholic solution.

The pure tetramethylorthosulphaminebenzamide yielded the following results on analysis:

I. 0.2143 gram substance gave 0.2082 gram $BaSO_4$.

II. 0.1978 gram substance gave 0.1937 gram $BaSO_4$.

III. 0.2396 gram substance gave 0.4345 gram CO_2 and 0.1424 gram H_2O.

IV. 0.1851 gram substance gave 0.5162 gram CO_2 and 0.1703 gram H_2O.

V. 0.1590 gram substance gave 0.0195 gram N.

VI. 0.2508 gram substance gave 0.0285 gram N.

	Calculated for $C_6H_4\langle^{CON(CH_3)_2}_{SO_2N(CH_3)_2}$	Found. I.	II.	III.	IV.	V.	VI.
S	13.01	13.25	13.44	....	....	....	....
C	49.53	....	....	49.72	49.37	....	....
H	6.56	....	....	6.66	6.67	....	....
N	11.37	....	....	....	....	12.26	11.38

Unlike the esters of benzoic sulphinide, tetramethylorthosulphaminebenzamide is not changed by alcoholic caustic alkalies. Like the esters, it is not decomposed by dilute aqueous caustic alkalies. Concentrated aqueous alkalies give the corresponding salt of orthosulphobenzoic acid and dimethylamine:

$$C_6H_4\langle^{CON(CH_3)_2}_{SO_2N(CH_3)_2} + 2KOH = C_6H_4\langle^{COOK}_{SO_2OK} + 2NH(CH_3)_2.$$

Dilute mineral acids do not hydrolyze the compound.

A crystallographic examination[1] gave the following results:

[1] The crystallographic work herein described was done by Dr. H. B. Matthews and Mr. A. Johannsen.

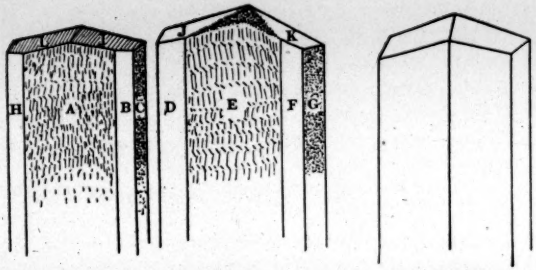


Fig. I. Fig. II. Fig. III.

The crystals were found to be of two habits, both tabular, parallel to the front pinacoid (100), but differing in the presence or absence of the front pinacoid. The crystals are simple and show but few faces. Figs. I. and II. are front and back views of the same crystal, and Fig. III. is of the other type.

Faces *A* and *E* were imperfect, showing many small cavities or incomplete growth. Faces *L* and *I*, which were striated parallel to the edge *LI*, were large and extended almost entirely across the crystals, giving them a monoclinic appearance. The edges *IB* and *LH* were so imperfect that they could not be used in measurements. Faces *J* and *K* were very small and their edges against the pinacoidal were indistinct, rendering measurements of these angles impossible.

The average of the angles observed were as follows:

HA, AB, DE, DF,	12° 30′.	Range of reading, 9′.
BC, CD, FG, GH,	77° 30′.	Range of reading, 17′.
BH, FD,	25° 00′.	
IJ,	60° 35′.	
JD,	44° 12′.	
CI,	73° 25′.	
IA, LA,	70° 21′.	
LI,	32° 10′.	

JE, KE, IB, and LA were indeterminate.

The foregoing measurements did not clearly prove the

monoclinic or orthorhombic character of the crystals, but optical tests showed parallel extinction with the emergence of a bisectrix in section parallel to *A*. The extinction shown when the crystal was examined parallel to *C* was also parallel. The plane of the optic axes was perpendicular to the tabular face. From the parallel extinction in two directions it is concluded that the crystals are orthorhombic, though the conclusion is neither proved nor disproved by the crystal measurements. On the assumption that the crystals are orthorhombic, the following crystallographic constants are found :

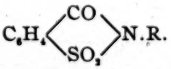
Axial ratio $a : b : c$. 0.232 : 1 : 0.127.

Action of Dimethylamine on the Unsymmetrical Chloride.— The only product of the action of dimethylamine on the unsymmetrical chloride that was isolated was the compound obtained from the symmetrical chloride and dimethylamine. No infusible product, corresponding to the primary amine derivative, was isolated.

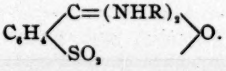
Summary.

This investigation has shown :

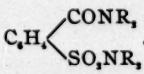
1. That the symmetrical chloride reacts with primary amines with the formation of the esters of benzoic sulphinide of the general formula,



2. That the unsymmetrical chloride with primary amines yields small amounts of the esters of benzoic sulphinide, together with infusible disubstituted amides :



3. That the secondary amines react normally with the symmetrical chloride, giving rise to compounds of the general formula,



IV. THE ACTION OF PHENOL ON THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

By Robert E. Humphreys.

In the year 1894, Remsen and Saunders[2] studied the action of phenol on what were then known as the solid and liquid chlorides of orthosulphobenzoic acid. When phenol was added to the mixed chlorides they passed into solution, but no reaction was observed to take place in the cold. On warming, the evolution of hydrochloric acid began at once, and the liquid assumed a clear, lake-red color, which became more intense as the reaction proceeded. When poured into a hot solution of dilute sodium hydroxide, a crystalline product separated which proved to be the diphenyl ester of orthosulphobenzoic acid, $C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases}$. When the solid chloride alone was employed, the same products were formed as with a mixture of the chlorides. The liquid chloride, when treated in the same way, showed the usual color reaction, and when the product was poured into dilute sodium hydroxide a heavy, yellow oil settled to the bottom of the vessel and became crystalline after a time. On recrystallizing this from alcohol two substances were isolated. One of these crystallized in needles and proved to be the diphenyl ester of orthosulphobenzoic acid, and the other crystallized in clear, thin columns, which melted at 98° to 100°. The latter product was not studied. The coloring-matter was supposed to be phenolsulphonephthalein.

In the following year Remsen and McKee[3] repeated this work. They obtained the diphenyl ester of orthosulphobenzoic acid without difficulty, but made no mention of finding the substance which melted at 98° to 100°. They tried the effect of treating the reaction-products with dilute ammonia instead of dilute sodium hydroxide. In this case the whole

[1] From the author's dissertation submitted, June, 1900, to the Board of University Studies of the Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

[2] This Journal, 17, 352.

[3] *Ibid.*, 18, 794.

mass became oily, but solidified when allowed to stand for some time. This, when crystallized from alcohol, yielded the diphenyl ester of orthosulphobenzoic acid, and a new substance which was called phenyl orthosulphaminebenzoate and given the formula $C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases}$. They described the crystals as feathery-shaped, and gave the melting-point as 131° to 132°. They were not able to isolate the substance that formed this amide with ammonia, but supposed it to be the orthosulphone chloride of phenyl benzoate, $C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases}$, formed according to the following equation:

$$C_6H_4\begin{cases}COCl\\SO_2Cl\end{cases} + C_6H_5OH = C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + HCl.$$

This, they thought, reacted with ammonia to form phenyl orthosulphaminebenzoate in the following manner:

$$C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + NH_3 = C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases} + HCl.$$

In an article by List and Stein[1] on the chlorides of orthosulphobenzoic acid, the authors make the following statement with reference to this phenyl orthosulphaminebenzoate obtained by Remsen and McKee:

"On the contrary, in spite of the most careful experiments, we have in vain attempted to obtain the phenyl ester of orthosulphaminebenzoic acid. According to our experiments, the ester does not seem to be capable of existence. We did not obtain it either by treating the reaction-product of phenol and the chloride with aqueous ammonia, or by bringing together the pure phenyl ester chloride with ammonia water."

In consequence of this statement, Prof. Remsen suggested the advisability of repeating the work of McKee and of making a careful investigation of phenylorthosulphaminebenzoate

[1] Ber. d. chem. Ges., 31, 1648.

and the orthosulphone chloride of phenyl benzoate. The results of this investigation are recorded in this paper.

Confirmation of the Work of Remsen and McKee.—Two and a half grams of the symmetrical chloride were heated with 2 grams (2 molecules) of phenol in a test-tube for five hours at 40° to 45°. The reaction proceeded very slowly and was accompanied by the formation of a red coloring-matter, phenolsulphonphthaleïn.[1] The reaction-products, while hot, were poured into a small mortar containing ordinary, dilute ammonia, and stirred with a pestle. The mass formed a thick, viscous liquid, which required at least an hour, and frequently, in repetition of this experiment, four to five hours to solidify. The hardened product was finely triturated, washed, dried, and dissolved in 30 cc. of 96 per cent alcohol. On cooling, the diphenyl ester of orthosulphobenzoic acid separated in fine needles. These were filtered off and the filtrate evaporated down to a volume of 6 cc. On standing, small, heavy, transparent crystals formed which melted at 130° to 131°, and after recrystallization at 131° to 132°. This product corresponded in every way to the phenyl orthosulphaminebenzoate described by Remsen and McKee.

The above experiment was varied in many ways, but the general results were always the same. If the reaction-products were allowed to cool and then poured into cold, dilute ammonia and washed with cold water the yield of phenyl orthosulphaminebenzoate was increased, but if treated with warm ammonia and washed with hot water it was considerably lessened. Working under the best conditions, 3 grams of diphenyl ester and 1 gram of phenyl orthosulphaminebenzoate were obtained from 5 grams of the symmetrical chloride.

Two and one-half grams of unsymmetrical chloride were heated with 2 grams of phenol for five hours at 40° to 45°. The reaction was more rapid than in the case of the symmetrical chloride, but in general it appeared to proceed in the same way. The mass was poured into dilute ammonia and then treated exactly as above. The diphenyl ester separated out of the solution in alcohol. The filtrate from this was con-

[1] Remsen and Sohon: This JOURNAL, 20, 263.

centrated and allowed to stand. None of the phenyl orthosulphaminebenzoate appeared. When the solution was brought almost to dryness a small quantity of oil separated which had a strong odor of phenol. No success ever attended the efforts to get phenyl orthosulphaminebenzoate by this process. The substance obtained from the symmetrical chloride gave the following analytical results:

I. 0.2973 gram substance gave 0.6098 gram CO_2 and 0.1075 gram H_2O.

II. 0.1678 gram substance gave 0.3455 gram CO_2 and 0.0625 gram H_2O.

III. 0.2428 gram substance gave 0.2028 gram $BaSO_4$.

IV. 0.5773 gram substance required 15 cc. standard sulphuric acid (1 cc. = 0.00256 gram N), less 2 cc. standard soda (1 cc. = 0.004125 gram N), Kjeldahl method.

	Calculated for $C_6H_4\langle^{COOC_6H_5}_{SO_2NH_2}$	Found. I.	II.
C	56.28	55.90	56.15
H	3.99	4.04	4.16
N	5.07	5.08	....
S	11.57	11.57	....

Formation of Phenyl Orthosulphaminebenzoate.—Remsen and McKee[1] did not isolate the substance that reacted with ammonia to form phenyl orthosulphaminebenzoate. A careful search was, therefore, made for it. The best yield was obtained when the symmetrical chloride and phenol were heated at 40° to 45°, and this was the temperature employed in the following experiments.

Two and one-half grams of the symmetrical chloride were mixed with 2 grams of phenol and heated for five hours at the temperature mentioned above. The mass was poured into a small mortar and rubbed up first with cold water and afterwards with boiling water. Most of the coloring-matter was thus removed. After solidification it was finely triturated, filtered off, dried, and dissolved in glacial acetic acid. By fractional crystallization three substances were isolated which melted at 118° to 119°, 103° to 104°, and 79°.5, respectively. The first proved to be the diphenyl ester of orthosulphoben-

[1] *Loc. cit.*

zoic acid, the second the orthosulphone chloride of phenyl benzoate, and the third an unchanged portion of the symmetrical chloride. The orthosulphone chloride of phenyl benzoate was treated in the cold with aqueous ammonia, but there was no evidence of the formation of phenyl orthosulphaminebenzoate.

Another portion of the symmetrical chloride was heated with phenol, as above, and the product washed with cold water only. On crystallizing from glacial acetic acid the same products were obtained as in the preceding experiment. Again, the reaction-products were poured, without washing, directly into glacial acetic acid. After twelve hours a mass of crystals separated, but there was no evidence of the presence of any substance except those mentioned above. The crystals were filtered off and the filtrate poured into water. An oily substance separated, which was extracted with ether, dried over calcium chloride, and allowed to stand. After some time a few crystals of the diphenyl ester appeared, but nothing else was ever obtained. This part of the work was rendered very difficult by the presence of red coloring-matter.

Thinking that perhaps both hot and cold water destroyed the substance that formed phenyl orthosulphaminebenzoate on treatment with ammonia, the products were poured into absolute ether and allowed to crystallize. The beaker containing the solution was kept in a desiccator; crystals formed slowly and were removed from time to time and carefully examined. This was continued until the solution evaporated completely. No substances other than those already mentioned were discovered.

It became clear that the phenyl orthosulphaminebenzoate must have been formed by the action of ammonia upon the symmetrical chloride that escaped reaction with phenol. The reaction between the chloride and phenol was never complete, even when the heating at 40° to 45° was continued for five hours. Occasionally, when the mass was not frequently stirred during the heating, considerable of the chloride remained unacted upon. It was possible that ammonia, in the

presence of phenol, would react upon this to form phenyl orthosulphaminebenzoate.

Two grams of phenol were dissolved in 25 cc. of dilute ammonia and to this 2.5 grams of symmetrical chloride were added. Reaction began at once. The chloride was converted into a thick oil, which settled to the bottom of the vessel, and the solution became quite warm. After stirring for some time the oil solidified. This was filtered off, dried, and crystallized from alcohol. A mass of fine needles separated out which melted at 118° and appeared to be the diphenyl ester of orthosulphobenzoic acid, and so proved to be when it was recrystallized and submitted to analysis. When the filtrate was evaporated somewhat, it yielded a crop of clear, thick crystals, which, on purification, melted at 131° to 132°, and were exactly similar in all respects to those obtained by former methods.

The analysis of the needles gave the following results:

I. 0.1582 gram substance gave 0.3722 gram CO_2 and 0.0631 gram H_2O.

II. 0.1919 gram substance gave 0.4519 gram CO_2 and 0.0712 gram H_2O.

	Calculated for $C_6H_4\langle^{COOC_6H_5}_{SO_2OC_6H_5}$	Found. I.	II.
C	64.37	64.16	64.21
H	3.98	4.46	4.13
S	9.05	8.65	....

The above reaction was brought about in various ways. The chloride was dissolved in phenol and dilute ammonia slowly added with stirring. In some cases the mixture was allowed to get hot, in others it was cooled with tap-water or with ice-water. Phenyl orthosulphaminebenzoate was always formed, but the best yield was obtained when the chloride was dissolved in phenol and ammonia added in only slight excess. The following equation expresses the reaction:

$$2C_6H_4\langle^{COCl}_{SO_2Cl} + 3C_6H_5OH + 5NH_3 =$$

$$C_6H_4\langle^{COOC_6H_5}_{SO_2NH_2} + C_6H_4\langle^{COOC_6H_5}_{SO_2OC_6H_5} + 4NH_4Cl.$$

Two grams of unsymmetrical chloride were treated as above with phenol and ammonia. The oily mass at first formed was stirred until it solidified. It was then filtered off and crystallized from alcohol. Needles of the diphenyl ester separated. When the filtrate was evaporated from the needles no phenyl orthosulphaminebenzoate was obtained. The unsymmetrical chloride could not be induced to yield this product, although the experiments were carried out under many conditions of temperature, and with variations of the order of mixing the ingredients. The unsymmetrical chloride is partly converted into the ammonium salt of orthocyanbenzenesulphonic acid, $C_6H_4\begin{cases}CN\\SO_2ONH_4\end{cases}$, and partly into the diphenyl ester of orthosulphobenzoic acid :

$$2C_6H_4\begin{cases}CCl_2\\SO_2\end{cases}O + 2C_6H_5OH + 6NH_3 =$$

$$C_6H_4\begin{cases}CN\\SO_2ONH_4\end{cases} + C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases} + 4NH_4Cl.$$

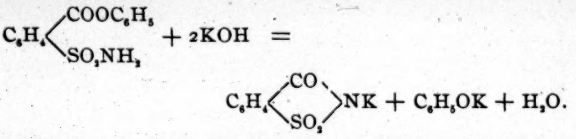
Properties of Phenyl Orthosulphaminebenzoate.—The melting-point is 132°. It is easily soluble in alcohol, acetone, and glacial acetic acid ; moderately soluble in benzene ; and difficultly soluble in ether, ligroin, hot water, and hot, dilute hydrochloric acid. The crystals are triclinic showing base, right and left prisms, and, occasionally, left negative pyramid, left brachydome, and macro-pinacoid. β is approximately 27°, α approximately 113°. γ was not determined. The basal cleavage is medium good, and luster vitreous. Medium index of refraction and low double refraction. Extinction + 5° 15′ off the right prismatic face on basal section.

Dilute potassium hydroxide readily converts it into the potassium salt of benzoic sulphinide.

Dilute ammonia acts in the same way. It is also slowly hydrolyzed by boiling water. It is soluble in hot water to an extent that permits of its purification by this means. The diphenyl ester of orthosulphobenzoic acid, the substance most

commonly contaminating it, is thus easily removed, as it is insoluble in hot water.

It is probable that the reaction proceeds according to the following equation:



Cresyl Orthosulphaminebenzoates.—It seemed desirable to try the action of the cresols on the chlorides of orthosulphobenzoic acid in the presence of ammonia in order to see if it is analogous to that of phenol. This was found to be the case. Only the ortho- and paracresols were employed. They reacted with more difficulty than phenol, and this was especially true of orthocresol. Both of the cresyl orthosulphaminebenzoates were prepared from the symmetrical chloride. The unsymmetrical chloride does not react with the cresols.

Orthocresyl Orthosulphaminebenzoate.–Two and one-half grams of symmetrical chloride are placed in a beaker with 1 gram of orthocresol and an excess of dilute ammonia. The whole is heated on the water-bath and vigorously stirred until the oily mass solidifies. This requires about ten minutes. The product must remain solid when heated up nearly to 100°. The chloride is thus converted into orthocresyl orthosulphaminebenzoate, and the dicresyl ester of orthosulphobenzoic acid, the former largely predominating. It is purified by recrystallization from alcohol. Its melting-point is 152°. On analysis the following results were obtained:

I. 0.1753 gram substance gave 0.1395 gram $BaSO_4$.

II. 0.1701 gram substance gave 0.1470 gram $BaSO_4$.

III. 0.3600 gram substance gave, by the Kjeldahl method, 0.0122 gram N.

IV. 0.3954 gram substance gave 0.01854 gram N.

	Calculated for $C_6H_4\langle^{COOC_7H_7}_{SO_2NH_2}$.	Found. I.	II.
S	11.01	10.92	11.58
N	4.82	4.78	4.69

Paracresyl Orthosulphaminebenzoate.—This is made by the method above mentioned. Paracresol reacts more easily than orthocresol, and the proportion of the dicresyl ester formed was much greater than in the preceding experiment.

It is impossible to say positively from a consideration of the foregoing reactions whether the amido group is in the benzoic acid or the sulphonic acid group, though they make it probable that it is the latter. In order to settle this question the following line of investigation was taken up. Orthosulphaminebenzoic acid, $C_6H_4\begin{cases}COOH\\SO_2NH_2\end{cases}$, and orthocarbaminesulphonic acid, $C_6H_4\begin{cases}CONH_2\\SO_2OH\end{cases}$, are both known, having been carefully investigated in this laboratory by F. D. Wilson.[1] It was proposed to make the phenyl esters of each of these acids and compare them with the phenyl orthosulphaminebenzoate, so-called, made by the action of phenol and ammonia on the symmetrical chloride.

Phenyl Orthocarbaminesulphonate.—Orthocarbaminesulphonic acid was made according to the method given by Wilson. This was converted into the chloride by heating the potassium salt with phosphorus oxychloride. The chloride is placed in a beaker with a little more than the calculated quantity of phenol and a slight excess of a dilute solution of potassium hydroxide. The whole is heated on a water-bath and stirred until the oily mass solidifies. It is then filtered off, carefully washed, and crystallized from alcohol. The crystals separate in the form of plates or needles. They are colorless and the melting-point is 95°. The product obtained as above gave the following analytical results:

I. 0.1502 gram substance gave 0.1322 gram $BaSO_4$.

II. 0.1231 gram substance gave 0.1059 gram $BaSO_4$.

III. 0.3866 gram substance gave, by the Kjeldahl method, 0.0206 gram N.

IV. 0.4098 gram substance gave 0.0216 gram N.

[1] Dissertation, 1899.

	Calculated for $C_6H_4\langle^{CONH_2}_{SO_2OC_6H_5}$	Found. I.	II.
S	11.57	12.11	11.81
N	5.07	5.32	5.27

The method of formation clearly indicates that the correct formula of this substance is $C_6H_4\langle^{CONH_2}_{SO_2OC_6H_5}$. It is entirely different from the substance obtained from the symmetrical chloride by treating with phenol and ammonia. Its melting-point is 37° lower, and its mode of crystallization quite different. Toward most of the reagents that easily act upon the phenyl orthosulphaminebenzoate it is stable. It resists the action of hot, dilute potassium hydroxide to a far greater degree, and is not converted by it into a salt of benzoic sulphinide.

Phenyl Orthosulphaminebenzoate.—The attempt was next made to prepare the phenyl ester of orthosulphaminebenzoic acid, $C_6H_4\langle^{COOC_6H_5}_{SO_2NH_2}$. The acid was prepared according to directions given by Wilson.[1] Wilson was not able to make the chloride of this acid, and our attempts were also unsuccessful. Thinking that the ester might be made by direct treatment of the acid or its salts, various methods were tried. The acid was warmed with phenol and phosphorus oxychloride gradually added. A vigorous reaction resulted, but no ester was formed. The acid was transformed into benzoic sulphinide. When phosphorus pentachloride was employed instead of the oxychloride the result was the same. Then a mixture of the acid (1 part), phenol (4 parts), and concentrated sulphuric acid (0.2 part) was heated on the water-bath for eight hours. At intervals of one hour small portions were removed and examined for the ester. It was found that the formation of benzoic sulphinide began immediately and continued slowly to complete reaction. No evidence of the formation of the ester was found. The silver salt of the acid was prepared and heated with phenyl iodide at 125° for three

[1] *Loc. cit.*

days. As far as could be discovered, little or no reaction had occurred. Further efforts to prepare this ester were abandoned for lack of time. While it was not possible to prepare and compare it with the one formed by treatment of the symmetrical chloride with phenol and ammonia, yet the formula previously assigned to the latter substance, $C_6H_4\begin{cases}COOC_6H_5\\SO_2NH_2\end{cases}$, is rendered very probable by the fact that the phenyl ester of orthocarbaminesulphonic acid was shown to be quite a different substance. Other considerations pointing to the correctness of this view will be taken up in the general discussion of results.

Orthosulphone Chloride of Phenylbenzoate.—This substance is formed from both chlorides by heating them with phenol. In order to determine its proportion relative to that of the diphenyl ester of orthosulphobenzoic acid formed at the same time, the following experiments were undertaken: Two and one-half grams of each chloride were placed in a test-tube with 2 grams of phenol and heated five hours in a sulphuric acid-bath. A series of six experiments was made with each chloride at each of the following temperatures: 40° to 45°, 65° to 70°, 100°, and 135°.

At 40° to 45°, the lowest temperature at which reaction appeared to take place, the reaction proceeded very slowly and was never complete with either chloride at the end of five hours. The red mass formed was poured into a mortar and rubbed successively with cold and with hot water until the coloring-matter was removed as far as possible. This could not be completely effected, even by washing with dilute alkali. When poured into water the reaction-products form an oil which, as the washing proceeds, passes through a viscous stage to the solid state. This was then finally triturated, filtered off, and dried. The product from the symmetrical chloride had a pale-yellow color, and that from the unsymmetrical was nearly white. These were crystallized from glacial acetic acid. From the symmetrical chloride the diphenyl ester of orthosulphobenzoic acid, and the orthosulphone chloride of phenyl benzoate were

formed, the former in much greater quantity than the latter. The diphenyl ester crystallizes in needles, and the orthosulphone chloride of phenyl benzoate in heavy prisms. These could be roughly separated by the method of subsidence, but only an approximate determination could be made of the relative quantities present.

From the unsymmetrical chloride, the orthosulphone chloride of phenyl benzoate was formed almost exclusively, only a few needles of the diphenyl ester appearing.

At 60° to 65° the reaction-products were more highly colored and more difficult to wash free of coloring-matter. Some color remained even after most vigorous methods were used to remove it. When poured into a mortar and water added, each solidified at once without passing through the oily-viscous stages. The washed product from the symmetrical chloride had a light-yellow color, while that from the unsymmetrical was pink. The same products were formed as at the lower temperature, but in somewhat different proportions. From the symmetrical chloride the diphenyl ester was formed in larger quantity, the phenyl ester chloride in smaller. The same was found to be true in the case of the unsymmetrical chloride.

At 100° the products from the symmetrical chloride were a very small quantity of phenyl ester chloride and a relatively larger quantity of diphenyl ester. From the unsymmetrical, these two products were formed in about equal proportions.

At 130° the product from each chloride consisted wholly of diphenyl ester.

Taking these facts into consideration, the best method of preparing the orthosulphone chloride of phenyl benzoate is as follows:

One molecule of unsymmetrical chloride is heated with 2 molecules of phenol from twelve to sixteen hours at 40° to 45°. The mass is washed thoroughly with hot water, allowed to solidify, and crystallized from glacial acetic acid. The crystals are large and colorless and melt at 103° to 104°. When crystallized from alcohol they have the appearance of rhombs. It is easily soluble in alcohol and glacial acetic acid, and

difficultly soluble in ether and benzene. The substance prepared as above, gave the following results on analysis:

I. 0.1868 gram substance gave 0.3600 gram CO_2 and 0.0611 gram H_2O.

II. 0.2257 gram substance gave 0.4386 gram CO_2 and 0.0666 gram H_2O.

III. 0.1845 gram substance gave 0.3522 gram CO_2 and 0.520 gram H_2O.

IV. 0.1522 gram substance gave 0.1175 gram $BaSO_4$ and 0.0761 gram AgCl.

V. 0.1426 gram substance gave 0.1101 gram $BaSO_4$ and 0.0714 gram AgCl.

	Calculated for $C_6H_4\langle^{COOC_6H_5}_{SO_2Cl}$	Found. I.	II.	III.
C	52.62	52.56	52.99	52.06
H	3.04	3.63	3.29	3.14
S	10.79	10.64	10.59	....
Cl	11.97	11.68	12.37	....

Action of Acids, Water, Alkalies, Etc., upon the Phenyl Ester Chloride.

Dilute hydrochloric and *sulphuric acids* readily saponify the ester chloride when boiled with it, giving *o*-sulphobenzoic acid.

Water causes about the same decomposition when boiled with it for six hours.

The phenyl ester chloride was boiled with a solution of barium hydroxide which was saturated at the ordinary temperature. After two hours the thick, oily drops floating about in the solution solidified in a crystalline condition, and further boiling produced no change. The solid was filtered off, washed, and crystallized from alcohol. Fine needles separated which melted at 118° and had the well-known appearance of the diphenyl ester of orthosulphobenzoic acid. The filtrate yielded crystals of barium orthosulphobenzoate.

I. 0.1875 gram substance gave 0.1171 gram $BaSO_4$.

II. 0.1946 gram substance gave 0.1210 gram $BaSO_4$.

	Calculated for $C_7H_4SO_5 + 2H_2O$.	Found. I.	Found. II.
Ba	36.79	36.76	36.59

The needles gave the following analytical results for carbon and hydrogen:

I. 0.1752 gram substance gave 0.4115 gram CO_2 and 0.0635 gram H_2O.

II. 0.1973 gram substance gave 0.4600 gram CO_2 and 0.0704 gram H_2O.

	Calculated for $C_6H_4\begin{cases}COOC_6H_5\\SO_2OC_6H_5\end{cases}$	Found. I.	Found. II.
C	64.39	64.06	64.05
H	3.98	4.03	3.96

The formation of the diphenyl ester under these conditions was unexpected, although it is easily explained as a special form of the Schotten-Baumann reaction:

$$2C_6H_4\begin{cases}COOC_6H_5\\SO_2Cl\end{cases} + 2Ba(OH)_2 =$$

$$C_6H_4\begin{cases}CO_2\\SO_2\end{cases}Ba + BaCl_2 + C_6H_4\begin{cases}CO_2C_6H_5\\SO_2C_6H_5\end{cases} + 2H_2O.$$

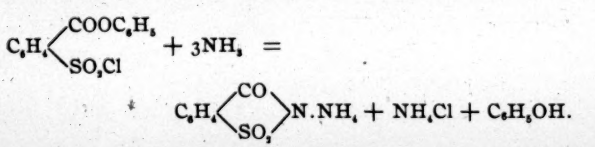
A similar experiment was carried out with a solution of potassium hydroxide. There was a gradual formation of the diphenyl ester, which continued for two hours, when the reaction was complete. The other product of the reaction was orthosulphobenzoic acid. No constant quantitative relations between these products were discovered in this or the preceding experiment.

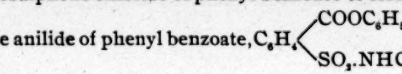
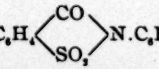
Aqueous *ammonia* acts only slightly on the orthosulphone chloride of phenyl benzoate in the cold, but when the temperature is raised the reaction proceeds very smoothly with the formation of the ammonium salt of benzoic sulphinide.

One gram of the substance was dissolved in absolute ether and the solution placed in a small cylinder, which was kept cool with ice-water. Dry ammonia gas was slowly passed through this for an hour. A white precipitate gradually

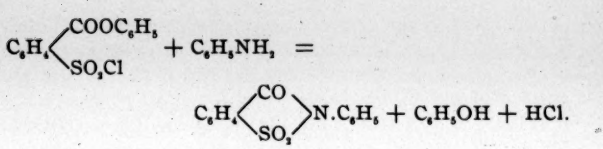
formed, and this was filtered off and dried. When dissolved in a small amount of water, this gave a precipitate of benzoic sulphinide on the addition of strong hydrochloric acid.

The above experiment was repeated and the ether kept at a temperature of 30°. The reaction took place essentially as before. The phenyl ester chloride in solution in ether is decomposed by ammonia according to the following equation:

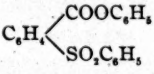


Action of Aniline.—It was thought that aniline would react with the orthosulphone chloride of phenyl benzoate to form the orthosulphone anilide of phenyl benzoate,  . Finely powdered orthosulphone chloride of phenyl benzoate was added to an emulsion of aniline in water. An oily mass was formed which slowly solidified. The solid was freed from aniline by washing, first with dilute hydrochloric acid and then water. On crystallizing from glacial acetic acid, unchanged phenyl ester chloride first separated, and afterwards a small quantity of long, white blades which melted at 190° to 191°. They were insoluble in water and alkalies, and proved to be the anil,  , described by Remsen and Coates.[1] When the substance was treated with pure aniline, the yield of the anil was quite good. No evidence of the formation of the orthosulphone anilide of phenyl benzoate was observed. Finally, some phenyl ester chloride was dissolved in ether, and to this was added a solution of aniline in ether. The reaction was very slow. Only the anil in small quantity was formed.

[1] This JOURNAL, 17, 311.



An attempt was made to prepare the compound



from the ester chloride by means of the reaction of Friedel and Crafts, but the attempt was unsuccessful.

Five grams of the substance were placed in a small flask connected with an inverted condenser and boiled with absolute alcohol for twelve hours. The alcohol was distilled off and the residue heated on the water-bath to expel the last traces of hydrochloric acid. This residue had a strong odor of phenol. A small quantity of water was added and the solution neutralized with barium carbonate. The filtrate from the excess of the carbonate was evaporated to a small volume and a few cubic centimeters of alcohol added. On standing, very fine needles separated out. These were filtered off, washed with alcohol, and dried. Analysis gave the following results:

I. 0.3906 gram substance lost 0.0044 gram when heated to 150°.

II. 0.1035 gram substance gave 0.0500 gram $BaSO_4$.

III. 0.3239 gram substance gave 0.1557 gram $BaSO_4$.

IV. 0.2437 gram substance gave 0.1171 gram $BaSO_4$.

		Found.	
Calculated for	I.	II.	III.
Ba	28.42	28.29	28.28

This substance was not fully identified and needs further investigation.

Action of Phenol in the Presence of Dilute Potassium Hydroxide.—As was mentioned in a previous part of this paper, when the attempt is made to saponify the orthosulphone chloride of phenyl benzoate with alkalies, the reaction is always

accompanied by the formation of diphenyl ester of orthosulphobenzoic acid. This suggested the following experiments:

One gram of the orthosulphone chloride of phenyl benzoate was boiled with an excess of phenol and dilute potassium hydroxide. In a short time the oily mass first formed solidified. This was filtered off and crystallized from alcohol. Needles of the diphenyl ester separated and this was the sole product. The reaction was smooth and rapid.

One gram each of the symmetrical and unsymmetrical chlorides were treated with phenol and the smallest possible excess of dilute potassium hydroxide in the cold. The viscous masses first formed were stirred until they solidified. On crystallization from glacial acetic acid it was found that nothing but the diphenyl ester was formed from the symmetrical chloride, but both diphenyl ester and the orthosulphone chloride of phenyl benzoate were formed from the unsymmetrical, the latter in larger quantity than the former. When care is taken to keep the temperature low, the phenyl ester chloride can be obtained in nearly pure condition by means of this reaction. It is a convenient and rapid method for preparing all the members of this class of compounds. When the method of heating the chlorides with phenol is employed the process is long and coloring-matters are formed at the same time that are extremely difficult to remove. All this is avoided by the method just described.

When the temperature is allowed to rise during this reaction the diphenyl ester alone is formed.

Action of the Cresols on the Chlorides of Orthosulphobenzoic Acid.—One gram each of the symmetrical and unsymmetrical chlorides were heated with 1 gram of orthocresol at 60° to 65° for two days. This was the lowest temperature at which a fairly good reaction would take place. Even at this temperature it was necessary to heat for two days to obtain a good yield. Coloring-matter was formed in large quantity with each chloride and was very hard to remove. The solid product was crystallized from glacial acetic acid. From the symmetrical chloride nothing definite could be isolated. From the unsymmetrical the orthosulphone chloride of orthocresyl benzoate

was obtained. This crystallizes in rhomb-like forms and melts at 112°. The substance was analyzed with the following results:

I. 0.2513 gram substance gave 0.1133 gram AgCl.
II. 0.2360 gram substance gave 0.1112 gram AgCl.
III. 0.2994 gram substance gave 0.2281 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COOC_7H_7}_{SO_2Cl}$	Found. I.	II.
Cl	11.41	11.15	11.64
S	10.32	10.46	....

When the chlorides were treated with orthocresol and dilute potassium hydroxide the unsymmetrical goes over easily into the orthosulphone chloride of orthocresyl benzoate. The symmetrical is decomposed by the alkali without the formation of this substance or the diorthocresyl ester to any considerable extent. Only a few crystals of the latter were obtained. These had the form of needles, resembling somewhat the crystals of the diphenyl ester (m. p. 141°). The difficulty encountered in the formation of this ester must be due to the protective influence of the group in the ortho position. The diphenyl ester is formed with the greatest ease by this method, and the diparacresyl ester is also obtained without trouble.

The orthosulphone chloride of paracresyl benzoate is obtained by heating the unsymmetrical chloride with paracresol, or by treating it with paracresol and dilute potassium hydroxide. Some diparacresyl ester is obtained at the same time if the temperature in either case is high. The symmetrical chloride, under the same treatment, yields diparacresyl ester.

ON RELATIONS BETWEEN THE COLOR AND THE COMPOSITION AND CONSTITUTION OF THE ALKALI SALTS OF THE NITROPHENOLS.

By J. C. W. Frazer.

The alkali salts of the nitrophenols, so far as they have been made, show quite a wide variation in color, and this

difference of color has been studied by Carnelly and Alexander[1] in the case of the sodium and potassium salts of ortho- and paranitrophenol. Since this work of Carnelly and Alexander the subject has not been further investigated and in some cases, notably in the case of metanitrophenol, the number of salts is extremely small. In none of them has either the rubidium or caesium salt been made.

At the suggestion of Professor Remsen I have prepared the sodium, potassium, rubidium, and caesium salts of the three nitrophenols, the object being to see if any connection between their color and composition could be discovered. The salts of these metals were chosen as furnishing the best series for such a study. Of metanitrophenol only the potassium salt is recorded. As the work progressed, 1 : 2 : 3 nitrocresol was included in the list of substances whose salts were made and analyzed.

Ortho- and paranitrophenol were made in the usual way by treatment of phenol with nitric acid, and after separating the oily layer from the acid the orthonitrophenol is distilled off with a current of steam. As the orthonitrophenol comes over in this operation it is sufficiently pure for use. The paranitrophenol is extracted from the tarry mass by hot, strong hydrochloric acid, and this solution boiled with animal charcoal. It is obtained perfectly pure by several recrystallizations in this manner.

Metanitrophenol was obtained from metanitraniline by first diazotizing and boiling the resulting diazo compound with dilute sulphuric acid, and then extracting this solution with ether. During this operation the directions of Bantlin[2] were followed. By recrystallizing from strong hydrochloric acid, as in the case of paranitrophenol, the substance is obtained pure.

In making the 1 : 2 : 3-nitrocresol, orthotoluidine is the starting-point. From this, orthocresol was made. By treatment of the orthocresol with nitric acid in acetic acid solution, action takes place at once,[3] and after standing a short while

[1] J. Chem. Soc., 4, 64.
[2] Ber. d. chem. Ges., 11, 2099.
[3] *Ibid.*, 14, 567.

the whole is poured into water. A brownish-red substance separates out, and from this, by distillation with steam, the 1 : 2 : 3-nitrocresol passes over while the 1 : 2 : 5-nitrocresol, which is formed at the same time, is left behind. In this condition the substance is not quite pure enough for use, but it can be obtained pure by recrystallizing from dilute alcohol. It then melted sharply at 69°.5.

The preparation of the nitrophenolates is a simple matter as they can be obtained from either the carbonates or the hydroxides. In making the nitrocresolates it is best to use the hydroxide of the metal, as the substance is such a weak acid that it is necessary to heat for some time to drive out carbon dioxide completely from carbonates, and this is objectionable on account of the volatility of the nitrocresol with water vapor.

Some of these salts are obtained in pure state only with difficulty. This was found to be true of sodium and caesium orthonitrophenolate and of some of the nitrocresolates. This is probably due to the fact that the salt in solution undergoes slight decomposition while evaporating, and some of the nitrophenol or nitrocresol separates with the salt. That slight decompositions do take place in solutions of these salts is indicated by the fact that the odor of orthonitrophenol and nitrocresol can be observed when the solutions have stood for any length of time. The dry salts too undergo very slow decomposition, the orthonitrophenol and nitrocresol escaping and the substance turning white. This may be due to the tendency of the carbon dioxide of the atmosphere to convert the substances into carbonates.

In order to purify those salts which separated in slightly impure condition, the following method was adopted: The salt was treated in the cold with strong alcohol to free it from any excess of the nitrophenol or nitrocresol. It was then dissolved in hot alcohol, which would leave behind any excess of carbonate. The salt thus extracted was recrystallized from water. The analysis was made as soon as possible, because of the fact that some of the salts undergo slight decomposition on long standing, even when in tightly-corked bottles, as indicated by the odor.

The water of crystallization was not determined, as in some cases decomposition was found to take place. The metal was determined as sulphate and the formula deduced from these results.

Orthonitrophenolates.

Sodium Orthonitrophenolate.—With this salt concordant results could not be obtained till the method of purification outlined above was applied. Analyses made with each sample were concordant but varied with the sample used. This is shown by the following analyses:

Amount of substance taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.
0.5284	0.2178	13.35
0.7593	0.3116	13.26
0.5189	0.2250	14.04
0.5224	0.2246	13.94
0.5768	0.2348	13.22
0.3283	0.1388	12.90
0.4749	0.1976	13.47
1.0314	0.4429	13.90
1.4349	0.6115	13.80
0.8945	0.3194	14.0
0.9554	0.3389	13.94

Six different samples were made, and in the analyses above recorded the first and second were of one of these samples, the third and fourth of another, the fifth and sixth of another, the seventh of another, the eighth and ninth of another, the tenth and eleventh of another, and in all of them the percentage of sodium is too small for the anhydrous salt. By purifying the salt by the method above the following results were obtained:

Amount of substance. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.3805	0.1679	14.29	14.28
0.3511	0.1537	14.18	....

This agrees with the formula $C_6H_4\begin{cases}NO_2\\ONa\end{cases}$. The salt crys-

tallizes, as is well known, in large, splendid, scarlet-red needles, often as much as 2 cm. in length.

Potassium Orthonitrophenolate.—It is not as difficult to obtain this salt pure as it is to obtain the sodium salt above. It crystallizes from water solution in large, orange-red plates, often as much as a centimeter in length, or in orange-red needles which have been obtained as much as 3 cm. long. This salt has been made and analyzed by Fritzsche,[1] who, from his analysis, assigned to it the formula

$$C_6H_4\begin{cases}NO_2\\OK\end{cases}.\tfrac{1}{2}H_2O,$$

and later was made by Post and Mehrtens,[2] who gave it the formula $C_6H_4\begin{cases}NO_2\\OK\end{cases}.H_2O$. The analyses of this salt made by myself agree with the formula first given it by Fritzsche, as will be seen:

Amount of salt taken. Grams.	K_2SO_4 found. Gram.	K found. Per cent.	Calculated. Per cent.
1.1583	0.5387	20.86	20.96
1.1251	0.5230	20.83	....

Rubidium Orthonitrophenolate.—This salt has not been described. It crystallizes from water in large, beautiful plates resembling very much the corresponding potassium salt above, except that it is slightly lighter in color than this salt. It crystallizes well in orange-yellow crystals, which have a composition analogous to the corresponding potassium salt. It is to be represented by the formula $C_6H_4\begin{cases}NO_2\\ORb\end{cases}.\tfrac{1}{2}H_2O$.

Amount of substance taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.4010	0.2297	36.67	36.74
0.4563	0.2611	36.62	....

As will be seen later, this is the usual form in which the

[1] Ann. Chem. (Liebig), 110, 153.
[2] Ber. d. chem. Ges., 8, 1552.

salt crystallizes, but not the only one. There is another variety of this salt and the passage of this last into the more common variety is an interesting one. Of this I shall speak more fully later on.

Caesium Orthonitrophenolate.—This salt has not been previously described. It is very soluble in water but crystallizes from this strong solution in large crystals, having in this respect the tendency, shown by the orthonitrophenolates above, of crystallizing well. It can be obtained pure only with difficulty. The two following analyses, made with different samples, show this :

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.
0.4341	0.2782	47.06
0.2992	0.1931	47.43

On purification by the method adopted above, the following results were obtained :

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2990	0.1994	48.99	49.07
0.2829	0.1890	49.09	....

This salt differs in crystalline form from the other orthonitrophenolates above described. It crystallizes neither in needles nor in plates, but in thick, massive crystals of a dark scarlet-red color, resembling sodium orthonitrophenolate. By reflected light the crystal faces show a slightly greenish color.

In this series of four orthonitrophenolates, two crystallize without water of crystallization and two with 0.5 molecule of water each. The first two, sodium and caesium orthonitrophenolates have, so far as I have ever noticed, no tendency to crystallize with water of crystallization. On the other hand, it has been found possible to crystallize potassium and rubidium orthonitrophenolate without water of crystallization. Fritzsche had early remarked on the difference in color between sodium and potassium orthonitrophenolate, and had actually tried to obtain the potassium salt in the dark-red variety corresponding to the sodium salt. He tried to do this by crystallizing the salt from alcohol, but found that even from absolute alcohol

the salt crystallized in the lighter form and still contained 0.5 molecule of water of crystallization.

On crystallizing the rubidium salt from water it was observed that at times it would crystallize out in dark-red needles, resembling the sodium salt very much, though it was not quite so dark as the latter. On setting the beaker down, the salt in contact with the mother-liquor began to change to the lighter, ordinary variety of the salt. On dissolving the salt by warming the solution, it came down again in the dark variety. But it was found that the salt in this form had such a tendency to pass over into the lighter variety as to make it impossible to filter it off and obtain it in dry condition. When slightly disturbed by touching it with a stirring rod, the change begins at the point of disturbance and passes over the whole mass of crystals. Further, the change can be brought about by sprinkling a small amount of the lighter crystals on the red crystals when they have separated out from the solution. By considering the colors of the orthonitrophenolates described above we might suppose this darker variety of the rubidium salt to be anhydrous like the sodium and caesium salts, which it resembles in color, the change of color being brought about by the change of the salt to the hydrated condition, which is the usual condition in which it separates from water solution.

In order to obtain the salt in pure condition then, if this were true, it would be necessary to exclude water from the solvent used. For this purpose absolute alcohol was chosen as the best solvent. Crystallization was effected from absolute alcohol, but as the time for evaporation at ordinary temperature is so great that the substance begins to change because of absorbing atmospheric moisture, the evaporation was hastened by keeping the solution warm. Under these conditions the salt crystallizes out in red needles, lighter in color than sodium orthonitrophenolate but much darker than the common variety of rubidium orthonitrophenolate. The salt has the formula $C_6H_4\begin{cases}NO_2\\ORb\end{cases}$, as seen from the following analysis :

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.2331	0.1397	38.39	38.23

That the increased temperature can have nothing to do with the change of color is shown by the fact that the same result can be obtained without the aid of heat, by simply causing the evaporation to take place in a dry atmosphere.

I have obtained sodium, rubidium, and caesium orthonitrophenolates in the dark-red variety. The potassium salt alone, of those investigated here, remains and under ordinary circumstances shows no tendency to crystallize in the darker variety. It was this salt which Fritzsche[1] had tried to crystallize in the darker variety. For this purpose he crystallized it from absolute alcohol and presumably in an open vessel. He found that the substance always crystallized in the lighter variety and always contained 0.5 molecule of water.

In using the same solvent as Fritzsche had used, it was soon found that alcohol simply distilled over quicklime still contained enough water to transform the salt, at least to some extent, into the hydrate, so that alcohol which had been distilled over sodium was used. Some potassium orthonitrophenolate was dehydrated by heating in an air-bath to 120°, dissolved in hot, absolute alcohol, and quickly filtered into an Erlenmeyer flask while still hot. The flask and its contents were kept almost at its boiling-point, and air, dried by passing through two wash-bottles containing sulphuric acid, was drawn through the flask. The crystals which separated at first were red and very much like the darker rubidium salt above. As evaporation went on the crystals, which had separated, began to turn lighter, and before evaporation was complete, only the yellow variety remained. The red variety of this salt was not obtained pure until evaporation of the solution was effected in a current of air dried over phosphorus pentoxide. Under these circumstances, the salt crystallizes from absolute alcohol in small, red needles, similar in appearance to the rubidium salt obtained in a similar manner. The remarkable fact brought out by this experiment is that this

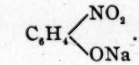
[1] Ann. Chem. (Liebig), 110, 153.

salt has the power to take up water from air dried over sulphuric acid. It was found by analysis to be the anhydrous salt as seen below:

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.1915	0.0935	21.88	22.00

Metanitrophenolates.

Sodium Metanitrophenolate.—This salt crystallizes in rather small needles of an orange-red color, resembling somewhat potassium orthonitrophenolate. It was found on analysis to have the composition represented by the formula



as seen below.

Amount of salt taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.2190	0.0771	11.41	11.6

Potassium Metanitrophenolate.—This salt, like sodium metanitrophenolate, crystallizes in small, needle-shaped crystals but are much lighter in color than the latter. They are orange-yellow. On analysis it was found to have the composition represented by the formula Post and Mehrtens[1] give it the formula

Amount of substance taken. Gram.	K_2SO_4 found. Gram.	K found. Per cent.	Calculated. Per cent.
0.3206	0.1206	16.89	16.88
0.2793	0.1059	17.03	....

Rubidium Metanitrophenolate.—Two salts of rubidium with metanitrophenol have been isolated, one the neutral salt, the other an acid salt. The difference in color between these two substances is very marked and is suggestive of the difference in color observed in the two forms of rubidium orthonitro-

[1] Ber. d. chem. Ges., 8, 1552.

phenolate above. But the difference here is due to another cause.

The lighter of the two is the neutral salt which was shown by analysis to have the formula $C_6H_4\begin{cases}NO_2\\ORb\end{cases}$. It crystallizes in small, yellow, needle-shaped crystals. Its analysis gave the following results:

Amount of substance taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.3459	0.2065	38.27	38.2

The acid salt mentioned above crystallizes in clusters of well-formed, needle-shaped crystals, radiating from a common point. They are of brownish-red color by transmitted light and brown by reflected light, and have the composition represented by the formula

$$C_6H_4\begin{cases}NO_2\\ORb\end{cases} + C_6H_4\begin{cases}NO_2\\OH\end{cases}.$$

The analysis gave the following results:

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.4031	0.1485	23.58	23.5

Caesium Metanitrophenolate.—This salt crystallizes in beautiful, almost blood-red crystals, which resemble caesium orthonitrophenolate in color, but the color is clearer and a more brilliant red. It is, like one of the rubidium salts above, an acid salt, having the composition represented by the formula $C_6H_4\begin{cases}NO_2\\OCs\end{cases} + C_6H_4\begin{cases}NO_2\\OH\end{cases}$, as seen from the following analytical results:

Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2854	0.1261	32.46	32.4

Paranitrophenolates.

Sodium Paranitrophenolate.—This salt crystallizes from

water in large, lemon-yellow prisms, which on standing exposed for even a short time lose their transparency and become opaque without any noticeable change of color. This change has been studied and found, as was to be expected, to be due to loss of water of crystallization. As the salt first crystallizes, it contains 4 molecules of water of crystallization, and on standing exposed to the air two of these are given off.

Potassium Paranitrophenolate.—This salt differs from the others by its lack of crystallizing power. On evaporating slowly it was found to come down as a lemon-yellow, crystalline powder. On analysis it was found to have the composition represented by the formula $C_6H_4\begin{cases}NO_2\\OK\end{cases}.H_2O$.

Amount of salt taken. Gram.	K_2SO_4 found. Gram.	K found. Per cent.	Calculated. Per cent.
0.2592	0.1172	20.26	20.0
0.2323	0.1052	20.29	....

This salt has been made and analyzed by Post and Mehrtens,[1] who found it to have the composition

$$C_6H_4\begin{cases}NO_2\\OK\end{cases}.2H_2O.$$

Rubidium Paranitrophenolate.—This salt crystallizes from water in large, bright-yellow scales having the composition

$$C_6H_4\begin{cases}NO_2\\ORb\end{cases}.H_2O.$$

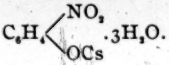
Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.2111	0.1161	35.2	35.3
0.2277	0.1250	35.14	....

Rubidium paranitrophenolate crystallizes from water in beautiful, well-formed, yellow needles, which, when filtered off, begin to break up at once into small parts, a change which may probably be due to loss of water of crystallization, as in the case of sodium paranitrophenolate. The rapidity of the

[1] Ber. d. chem. Ges., 8, 1552.

change made it impossible to obtain the substance in a state of sufficient purity for analysis.

Caesium Paranitrophenolate.—This salt crystallizes in large, lemon-yellow plates having the composition



Amount of salt taken. Gram.	Cs_2SO_4 found. Gram.	Cs found. Per cent.	Calculated. Per cent.
0.2234	0.1240	40.78	40.9
0.3371	0.1872	40.81	....

1 : 2 : 3-Nitrocresolates.

Nitrocresol is a weaker acid than the nitrophenols, and, being a volatile substance, its salts are more easily decomposed, and it is harder to obtain them pure. This seemed especially true of the caesium salt, solutions of which, when left to evaporate, underwent continuous decomposition with separation of nitrocresol. This may have been caused by the slow and continuous action of carbon dioxide of the atmosphere, the odor of nitrocresol being always noticeable from solutions of its salts. On account of the weak acid properties of nitrocresol its salts are made from the hydroxides of the metals, and the purification of the salts is the same as in the case of the nitrophenolates.

Sodium Nitrocresolate.—This salt crystallizes from water solution in small, light-red needles, having the composition given by the formula $C_6H_3(NO_2)CH_3.ONa.2H_2O$.

Amount of salt taken. Gram.	Na_2SO_4 found. Gram.	Na found. Per cent.	Calculated. Per cent.
0.4165	0.1398	10.85	10.90
0.3672	0.1243	10.90	....

Potassium Nitrocresolate.—This salt crystallizes in light-red scales, resembling the sodium salt above. Its color is slightly lighter, and it has the composition represented by the formula $C_6H_3(CH_3)(NO_2)OK.\frac{1}{2}H_2O$.

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.1752	0.0760	19.45	19.5
0.3233	0.1413	19.66	....

Rubidium Nitrocresolate.—This salt crystallizes in beautiful, cherry-red scales having a very high luster. By slow evaporation the salt is deposited in well-formed, monoclinic, diamond-shaped crystals of dark, cherry-red color. It has the composition $C_6H_3(CH_3)(NO_2)ORb.H_2O$.

Amount of salt taken. Gram.	Rb_2SO_4 found. Gram.	Rb found. Per cent.	Calculated. Per cent.
0.2127	0.1122	33.59	33.4

Caesium nitrocresolate was made but, as has been stated above, at each recrystallization partial separation of the nitrocresol took place so that the salt was not obtained pure enough for analysis. For some reason this salt was more unstable than the others. It is, however, of a red color, resembling sodium nitrocresolate in this respect.

The conductivity of ortho- and paranitrophenol has been determined by Hantzsch,[1] who gives the following tables:

Paranitrophenol (at 25°).

v.	μ_v. Per cent.
64	0.89
128	1.28
256	1.79
512	2.53

Orthonitrophenol (at 25°).

v.	μ_v. Per cent.
128	1.13
256	1.52
512	2.17
1024	3.14

These results differ considerably from those of Bader,[2] who found numbers considerably greater than these.

The determinations of my own, below, differ somewhat from those of Hantzsch and Schümann, but all of the three sets of determinations agree fairly well for a substance of such low conductivity, and they all show that orthonitrophenol is a slightly weaker acid than paranitrophenol, while metanitrophenol is a somewhat stronger acid than paranitrophenol.

Paranitrophenol (at 25°).

v.	μ_v. Per cent.
32	0.924
64	1.201
128	1.567
256	1.752

Melanitrophenol (at 25°).

v.	μ_v. Per cent.
32	1.18
64	1.20
128	1.52
256	2.01

Orthonitrophenol (at 25°).

v.	μ_v. Per cent.
128	1.02
256	1.85
512	2.38
1024	3.77

[1] Ber. d. chem. Ges., 32, 3066.
[2] Ztschr. phys. Chem., 6, 289.

From my own determinations, meta- and paranitrophenol are dissociated to about the same extent, while both are dissociated somewhat more than orthonitrophenol.

The absorption spectra of some of the salts of ortho- and paranitrophenol were examined but nothing of any apparent value was found. When in concentrated solution these substances were found to absorb all the violet end of the spectrum, even down through the yellow in the case of orthonitrophenolates. On diluting, more and more of the violet end of the spectrum was transmitted until, at great dilutions, only a diminution of the intensity of the violet end was noticed, without, at any time, a tendency to show a banded spectrum. The only difference in the case of solutions of paranitrophenolates is that the light is not absorbed so far down towards the red end of the spectrum as is the case with the same dilution of an orthonitrophenolate.

Carnelly and Alexander[1] have found :

(1) That without exception the color passes toward the red end of the spectrum as the temperature rises.

(2) That the color of the ortho compound is nearer the red end than the corresponding para compound. Para compounds have a higher melting-point than ortho compounds. The latter he concludes from this to be at a relatively higher temperature and according to this should have a color nearer the red end of the chromatic scale than the higher melting, para compound, which accords with the first conclusion above.

(3) By a comparison of the nitrophenolates of the same sub-group the color passes toward the red end as the atomic weight increases.

(4) The color passes toward the red end of the chromatic scale as the amount of water decreases.

Summary.

(1) Speaking in a general way concerning the color of the salts described above of the three classes of nitrophenolates, it may be said that the orthonitrophenolates possess a color that is nearest the red end of the chromatic scale, while the

[1] *Loc. cit.*

metanitrophenolates come next, and the paranitrophenolates are furthest removed from the red end.

(2) There is a gradation of color in the case of each series of nitrophenolates above, and in the direction pointed out in the third conclusion of Carnelly and Alexander above, that is, the color growing lighter in each series as the atomic weight of the metal increases. This, however, is not very noticeable in the paranitrophenolates as only little difference of color is observed in passing from one salt to the other in the series.

(3) In the same way, water of crystallization causes little change of color in the paranitrophenolates, while the change of color due to water of crystallization is greatest in the case of the orthonitrophenolates, and next in order in this respect come the metanitrophenolates.

(4) Paranitrophenol and metanitrophenol have the power of forming acid salts, while orthonitrophenol has not been found to have this power.

(5) The orthonitrophenolates above described are all red when dehydrated. This is also true of the metanitrophenolates though these are lighter than the orthonitrophenolates.

(6) Paranitrophenolates, with the exception of the sodium salt, are yellow when anhydrous and cold. The sodium salt is reddish.

(7) The nitrocresolates are all red, though not as dark as the orthonitrophenolates. In the case of the nitrocresolates, the variation in color from one salt to another is less than in the case of ortho- and metanitrophenolates. Water does not cause as great a change in the color of the nitrocresolates and of the paranitrophenolates as in the case of the other nitrophenolates.

JOHNS HOPKINS UNIV.,
June, 1901.

COMPARATIVE STUDY OF THE METASULPHAMINEBENZOIC ACIDS MADE BY DIFFERENT METHODS.

BY J. C. W. FRAZER.

Metasulphaminebenzoic acid has been made by several workers and by several methods, and the lack of agreement

which is found in their descriptions of the properties of the substance calls for a more careful study of the substance made in different ways. The point of greatest difference is in the melting-point which different investigators have found for the substance. Even when using the same method, different workers have found melting-points that differ quite markedly from one another. In fact, from these results it might fairly be doubted whether the same substance had always been under investigation, though the methods employed would leave little room for such doubt. For this reason, Professor Remsen suggested to me to prepare this substance by several methods and to determine whether the same product is always obtained and, so, to settle the question concerning its melting-point.

In view of the interesting influence which continued heating has been found to produce on parasulphaminebenzoic acid and of similar work that has been done in this laboratory on metasulphaminebenzoic acid itself, a definite statement concerning the melting-point of metasulphaminebenzoic acid acquires more than ordinary significance.

Metasulphaminebenzoic acid was first obtained by Limpricht and Uslar[1] from metasulphobenzoic diamide by heating with potassium hydroxide. Under these conditions the carbamine group is saponified and the sulphamine acid is precipitated on acidifying:

$$C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases} + KOH = C_6H_4\begin{cases}COOK\\SO_2NH_2\end{cases} + NH_3.$$

The authors describe the substance as separating in crystals resembling potassium chlorate. They did not determine its melting-point but found the substance to melt somewhere above 200°.

Remsen and Palmer[2] obtained the acid from metatoluenesulphone amide by oxidation with potassium permanganate. They found the substance they obtained to melt at 235° (uncorrected), at the same time suffering slight decomposition.

[1] Ann. Chem. (Liebig), 106, 36, 37, 42–46.
[2] This JOURNAL, 4, 144.

Noyes and Walker[1] have made the acid from metatoluenesulphone amide by oxidation with potassium ferricyanide. The potassium salt of the acid they obtained was washed with strong alcohol to remove any unoxidized amide. The acid liberated from this salt they found to have a melting-point of 246° to 247° (uncorrected).

W. Jones[2] has made the acid by three different methods: First, by a slight modification of the method of Limpricht and Uslar, when he obtained an acid melting at 248° (uncorrected). Next he obtained the acid by saponification of metasulphaminebenzoic nitrile with dilute caustic potash. The nitrile itself he obtained from the diamide by treatment with phosphorus pentachloride and, after distilling off the phosphorus oxychloride, crystallizing the product from warm water. The acid obtained in this way was the same as that from the first method above. Of the second method he says: "No method is better adapted to the preparation of the acid in pure condition than this one."

He obtained metasulphaminebenzoic acid by treatment of metasulphobenzoic chloride with aqueous ammonia. The acid obtained by this method he found to melt at 248° to 248°.5.

Griffin[3] obtained metasulphaminebenzoic acid by oxidation of metatoluenesulphone amide with chromic acid. On purifying, he obtained a substance melting at 233° (uncorrected).

Nakaseko,[4] working in this laboratory, next made the substance. He obtained the acid by the method recommended by Jones as being the best, the saponification of metasulphaminebenzonitrile. After recrystallizing the acid several times, he found it to melt at 237° to 238° (corrected). He then converted the acid into the ammonium salt and recrystallized this. The purified ammonium salt was converted into the lead salt and this in turn recrystallized several times. The acid was liberated from the lead salt by treatment with sulphuric acid and then recrystallized several times. During

[1] This JOURNAL, **8**, 188.
[2] Private communication.
[3] This JOURNAL, **19**, 180.
[4] Dissertation, 1898.

this treatment he found the melting-point had remained unchanged at 237° to 238°.

It was because of this variation that the following work was undertaken.

Metasulphobenzoic diamide was made from acid potassium metasulphobenzoate by treatment with phosphorus pentachloride. Metasulphobenzoic dichloride thus obtained is treated with aqueous ammonia when the diamide is obtained. This diamide is saponified with caustic potash by the method used by Jones, and the product acidified with hydrochloric acid. When the metasulphaminebenzoic acid crystallizes out the precaution mentioned by Jones is observed, that is, the solution is not allowed to become perfectly cold, otherwise the unchanged diamide separates along with the sulphamine acid. The substance thus obtained was recrystallized four times, observing the same precaution. This substance had a melting-point of 238°. When recrystallized a fifth time in the same way, after boiling with animal charcoal, the melting-point 237°.5 was obtained. Some of this product was then converted into the barium salt by treatment with barium carbonate and the barium salt recrystallized from water and repeatedly washed with 95 per cent alcohol, recrystallized, warmed with 95 per cent alcohol, and, after cooling, washed with alcohol and again recrystallized from water. From the salt thus purified the acid was liberated by treatment with hydrochloric acid, and the acid recrystallized from hot water. The metasulphaminebenzoic acid crystallized in beautiful, colorless scales, which melted at 237°.5 to 238° (corrected).

The metasulphobenzoic diamide above is then treated with phosphorus pentachloride, which converts it into metasulphaminebenzonitrile hydrochloride, $C_6H_4\begin{cases}C\overset{Cl}{\underset{NH}{<}}\\SO_2NH_2\end{cases}$, which, when dissolved in warm water, forms metasulphaminebenzoic nitrile, $C_6H_4\begin{cases}CN\\SO_2NH_2\end{cases}$. This substance is boiled five hours with di-

lute caustic potash. At the end of this time, on acidifying with hydrochloric acid, a voluminous precipitate separates which does not crystallize anything like the metasulphaminebenzoic acid. It can be separated by fractional crystallization into a crystalline portion, from which the sulphamine acid can be obtained in pure condition. Not a very good yield of the sulphamine acid was obtained, and the large amount of precipitate formed may have been the acid potassium salt which came down on acidifying, though this was not determined. After six recrystallizations the acid had every appearance of the metasulphaminebenzoic acid made by the method above, and was found to have the melting-point 237° to 238° (corrected).

Crude paratoluidinemetasulphonic acid was purified by boiling the solution acidified with hydrochloric acid and adding animal charcoal. Nitrogen trioxide was conducted into a thin paste made by mixing this with alcohol, according to the method given by Griffin.[1] The diazo compound thus obtained was decomposed in absolute methyl alcohol in presence of anhydrous sodium carbonate, according to the directions of the same author. After the decomposition of the diazo compound is complete, the alcohol is evaporated off, and the dried residue converted into metatoluenesulphone chloride by treatment with phosphorus pentachloride, and this, on treatment with aqueous ammonia, is converted into metatoluenesulphone amide. This amide was oxidized with chromic acid according to the directions given by Griffin. To free the acid formed from the unoxidized toluenesulphone amide, it is converted into the potassium salt. On liberating the free metasulphaminebenzoic acid and recrystallizing several times it was found to have all the appearance of that obtained by the methods above, and was found to have the melting-point 237°.5 to 238°.5 (corrected).

The metasulphaminebenzoic acid was next made from parabrommetatoluenesulphonic acid. The reduction of this acid has been accomplished by Müller[2] by treating its aqueous

[1] This JOURNAL, 19, 164.

[2] Ann. Chem. (Liebig), 169, 347.

solution with sodium amalgam. For the complete removal of the bromine the action is continued for about eight days. At the end of that time it is found that no bromine is left in the acid. The solution is then acidified with sulphuric acid and evaporated when, by allowing it to cool, a great deal of the potassium sulphate can be eliminated. The solution thus obtained from the sulphate, which has separated, is then evaporated to dryness and treated with phosphorus pentachloride. The oily chloride, after it has been washed with water, is converted into the amide by treatment with aqueous ammonia. The metatoluenesulphone amide thus obtained is oxidized with chromic acid as above, and the metasulphaminebenzoic acid obtained is purified in the same way. The substance had every appearance of that already obtained and melted at 237°.5 to 238° (corrected).

The acid was next obtained from the metasulphone chloride of benzoic acid, $C_6H_4\begin{cases}COOH\\SO_2Cl(m)\end{cases}$, by treatment with aqueous ammonia. This chloride was obtained from benzoyl chloride by treating it with sulphur trioxide. The sulphonic acid group enters the position meta to the carbonyl group, and by an action not yet understood the above substance is obtained. This, as stated, gives the metasulphaminebenzoic acid on treatment with aqueous ammonia and was found to melt at 237°.5.

The thermometer used in all this work was carefully compared with two standard thermometers and the corrections always applied.

There was one other point concerning the melting-point of this acid which was tested.

It is stated by Jones that his metasulphaminebenzoic acid could not be made to melt below 248°. He kept a small quantity of the acid at a temperature of 240° to 242° for an hour. The temperature was then gradually raised and while doing so was kept at temperatures from 242° to 246° for three hours, but the acid would not melt below 248°. On the other hand, Nakaseko found quite different results when proceed-

ing in a similar way. While he found the melting-point of the metasulphaminebenzoic acid to be 237° to 238° he says it can be melted considerably lower than this.

After drying the acid carefully in an air-bath at 140° for two hours, it was placed in specimen tubes and heated for four hours at 210° to 215°. At the end of this time it did not melt, but by raising the temperature slowly till it reached 220° it melted completely.

I placed about 1 gram of the dried metasulphaminebenzoic acid in a specimen-tube and heated it for one hour at 215° (once the temperature rose to 220° for a short time), and at the end of this time the substance had melted. This result is similar to that of Nakaseko, above referred to.

This being the case, in determining the melting-point of metasulphaminebenzoic acid made by the different methods above, the substance was heated as rapidly as possible till near the melting-point so as to avoid any change of the melting-point such as was found above to be caused by continued heating.

It will thus be seen that metasulphaminebenzoic acid, whether made (1) from metasulphobenzoic diamide, $C_6H_4\begin{cases}CONH_2\\SO_2NH_2\end{cases}$; (2) from metasulphaminebenzoic nitrile, $C_6H_4\begin{cases}CN\\SO_2NH_2\end{cases}$; (3) from the metasulphone chloride of benzoic acid, $C_6H_4\begin{cases}COOH\\SO_2Cl\end{cases}$;

(4) from parabrommetatoluenesulphonic acid,

$$C_6H_3\begin{cases}CH_3\\SO_3H(m)\\Br(p)\end{cases};$$

or (5) from paraminometatoluenesulphonic acid,

$$C_6H_4\begin{cases}CH_3\\SO_3H(m),\\NH_2(p)\end{cases}$$

is one and the same product. When heated rapidly it melts at 237° to 238° (corrected). When heated slowly it undergoes a change that causes it to melt as low as 215°.

JOHNS HOPKINS UNIV.,
June, 1901.

Contributions from the Sheffield Laboratory of Yale University.

CXI.—ON THE THIOCYANATES OF SILVER AND POTASSIUM AND THEIR SOLUBILITY.

BY H. W. FOOTE.

INTRODUCTION.

The main object of the present investigation has been to devise a method for determining what double salts are formed by two single salts with a common ion. The method depends chiefly on well-known principles of solubility.

The conditions regulating the solubility of two salts with a common ion are well known.[1] At a given temperature there will be but one saturated solution possible when both salts are present in excess, provided the salts form no double salts with each other. If one double salt AB forms from the two single salts A and B, there will be two definite saturated solutions, one when A and AB are both present as solids and the other when AB and B are present. The single salts alone or a double salt alone can exist in contact with a series of saturated solutions containing A and B. It follows that when two separate salts are present in the residue, the composition of this residue will change as the relative proportion of the two salts changes, but the composition of the saturated solution remains constant. When, however, only one salt, either simple or double, is in the residue, its composition must remain fixed while the composition of the saturated solution varies within certain limits. We have then the rule that if the composition of the residue varies in different determinations while the solution remains constant, a mixture of two salts is present. If the solution varies while the residue remains constant in composition, a single salt or one double salt is pres-

[1] Ostwald: Lehrb. d. allgem. Chem., **1**, 1076; Van 't Hoff: Vorles. über Bild. u. Spalt. von Doppelsalzen.

ent. The method of determining double salts by solubility determinations is based on this rule. A somewhat similar method has been used in investigating the periodides of caesium.[1]

The investigation has been carried out with the thiocyanates of silver and potassium. Their double thiocyanates have been prepared recently by Wells and Merriam,[2] who described the following compounds:

3KSCN.AgSCN, 2KSCN.AgSCN, and KSCN.AgSCN.

In testing the method on these salts, it has been shown that the salt 3KSCN.AgSCN is unstable under ordinary conditions of temperature. It readily passes over into a mixture of 2KSCN.AgSCN and potassium thiocyanate.

EXPERIMENTAL.

In carrying out the experimental work, accurately weighed quantities of potassium and silver thiocyanates were placed together in a strong glass tube, about the size of a test-tube, and treated with a known amount of water. The quantities of salt and water were so regulated that there was always an undissolved residue at the temperature of the experiment. The relative amounts of each salt were varied systematically in the different determinations. The mixtures were heated for some time, when possible, till both salts dissolved completely, and then placed in a Noyes solubility-apparatus at 25° C. After saturation had taken place, a small amount of solution was removed and analyzed. The composition of the residual thiocyanates could then be calculated with sufficient accuracy. This method of determining the composition of the undissolved salt could be used here, as it was known that all salts formed were anhydrous. In a case where salts contain water of crystallization, it would be necessary to analyze the residue instead of calculating its composition. In one or two cases this was done as a check on the calculated value. When the residue is analyzed, it is unnecessary to weigh ac-

[1] Foote: This JOURNAL, **29**, 203 (1903).
[2] *Ibid.*, **28**, 265.

curately the quantities of salts and water used in the experiments.

It should be mentioned that it was found difficult to saturate the solutions in which uncombined silver thiocyanate was present as solid phase. Constant results in this case were obtained only when the mixtures were kept at 25° for about a week, shaking them in the apparatus during the day.

The solutions were analyzed as follows: Weighed quantities of solution were treated with water, precipitating silver thiocyanate, which was filtered on a Gooch crucible, dried at 100° to 120° C., and weighed. A small quantity of ferric alum was added to the filtrate, which was acidified with nitric acid, and titrated with standard silver nitrate till just decolorized.

The results obtained are in Table I. Column I. gives the number of the experiment; Columns II. and III., the parts by weight of potassium thiocyanate and silver thiocyanate, respectively, in 100 parts by weight of solution; Columns IV. and V., the percentage of potassium thiocyanate and silver thiocyanate in the residue. The results are separated into groups whose significance will become apparent:

Table I.

I.	II. KSCN in solution.	III. AgSCN in solution.	IV. KSCN in residue.	V. AgSCN in residue.
1	70.38	....	100.0	....
2	70.68	....	100.0	....
3	66.44	9.46	87.95	12.05
4	66.80	8.95	74.29	25.71
5	66.42	9.56	55.25	44.75
6	64.47	10.62	53.38	46.62
7	61.25	11.76	53.97	46.03
8	58.34	13.55	54.23	45.77
9	53.21	17.53	54.14	45.86
10	50.55	20.46	49.12	50.88
11	50.81	20.40	43.98	56.02
12	49.43	20.32	36.58	63.42
13	32.51	18.34	36.75	63.25
14	24.68	16.41	36.26	63.74
15	23.89	16.14	32.83	67.17
16	23.83	16.01	24.66	75.34

Discussion of the Results.

In the above table, experiments Nos. 1 and 2 represent the solubility of pure potassium thiocyanate. Nos. 3, 4, and 5 show a constant solubility while the composition of the residue changes. This indicates that a mixture of potassium thiocyanate and the first double salt is present. Nos. 6, 7, 8, and 9 have a constant composition in the residue while the solution varies. Here the first double salt appears in pure condition. It is evidently 2KSCN.AgSCN. The pure salt contains 53.92 per cent of potassium thiocyanate. Nos. 10 and 11 have a constant solubility and variable composition of the residue corresponding to a mixture of 2KSCN.AgSCN and the next double salt. Nos. 12, 13, and 14 show variable composition of the solution while the residue corresponds closely to KSCN.AgSCN. The pure salt contains 36.90 per cent of potassium thiocyanate. Nos. 15 and 16 have a constant composition of the solution while the residue varies, corresponding to a mixture of KSCN.AgSCN and silver thiocyanate. The experiments were not carried beyond this point as unchanged silver thiocyanate could be seen in the residue.

The results in Table I. are shown graphically in Fig. I.

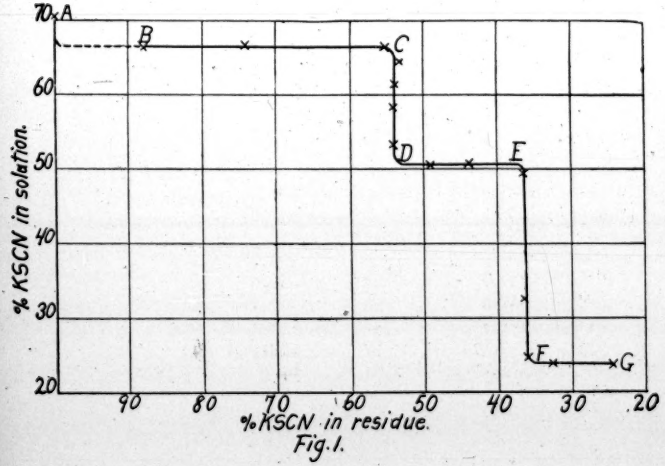


Fig. I.

The percentage of potassium thiocyanate in the solution is plotted as ordinate and the percentage of the same salt in the residue as abscissa. The point *A* represents the solubility of the pure salt. From *B* to *C* the solubility remains constant while the composition of the residue changes, corresponding to the mixture of potassium thiocyanate and 2KSCN.AgSCN. From *C* to *D* the solubility changes, while the residue consists of pure 2KSCN.AgSCN. *DE* shows a mixture of the two salts 2KSCN.AgSCN and KSCN.AgSCN in the residue. Along the curve *EF* only KSCN.AgSCN is present, while along *FG* this salt and silver thiocyanate are present.

The solubility results alone may be shown graphically without regard to the composition of the residue, by plotting the quantities of silver and potassium thiocyanates found in a definite quantity of water. For this purpose the solubility results in Table I. have been recalculated to obtain the molecules of potassium and silver thiocyanates in 100 molecules of water. Where two solids are present, giving a constant solubility, the average results have been used. These recalculated results are given in Table II. The numbers in the first column refer to the corresponding results in Table I.

Table II.—Solubilities Recalculated from Table I.

	Molecules KSCN in 100 molecules H_2O.	Molecules AgSCN in 100 molecules H_2O.
1, 2	44.36	0
3, 4, 5	51.13	4.19
6	47.98	4.60
7	42.07	4.72
8	38.47	5.23
9	33.71	6.50
10, 11	32.52	7.67
12	30.29	7.28
13	12.26	4.05
14	7.77	3.02
15, 16	7.36	2.90

These results are plotted in Fig. II. The molecules of potassium and silver thiocyanates in 100 molecules of water are plotted respectively as ordinate and abscissa.

The point *A* represents the solubility of pure KSCN.

The point *B* represents the solubility of KSCN and 2KSCN.AgSCN.

The point *C* represents the solubility of 2KSCN.AgSCN and KSCN.AgSCN.

The point *D* represents the solubility of KSCN.AgSCN and AgSCN.

The dotted lines indicate the solubility of potassium or silver thiocyanate when alone in the residue with varying amounts of both salts in solution.

The form of these curves was not directly determined.

The sharp changes in the direction of the curve in Fig. II. indicate the changes of the solid phase with sufficient clearness, but this method gives no clue as to what solid phase is present along any one curve.

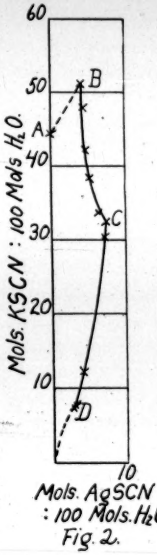


Fig. 2.

The objection might be raised to the solubility results which have been given, that the solubilities obtained were not what they would be in case the double salts themselves were used as a starting-point instead of the single salts. For the sake of comparison, solubility determinations were made in a few cases, using double salts which had previously been prepared, instead of the separate salts. The results are given in Table III., together with the average of the corresponding results taken from Table I.

Table III.

Solubility of KSCN with 2KSCN.AgSCN.

	Double salt and KSCN used.	Single salts used.
KSCN	66.46	66.65
AgSCN	9.60	9.32

Solubility of 2KSCN.AgSCN with KSCN.AgSCN.

	Double salts used.	Single salts used.
KSCN	50.91	50.68
AgSCN	20.41	20.43

Solubility of KSCN.AgSCN with AgSCN.

	Double salt and AgSCN used.	Single salts used.
KSCN	23.88	23.86
AgSCN	16.05	16.08

The results agree as well as would be expected.

The Unstable Salt 3KSCN.AgSCN.

The formation of the 2 : 1 and 1 : 1 double salts has been demonstrated conclusively by solubility experiments, but there has been no indication of the 3 : 1 salt. If this salt, containing 63.70 per cent of potassium thiocyanate had formed, the solubility in Experiments 3 and 4, Table I., in which the residues correspond in composition to a mixture of potassium thiocyanate and the 3 : 1 salt, would have been different from the solubility in Experiment 5, where the composition of the residue corresponds to a mixture of the 3 : 1 and 2 : 1 salts. There would also have been a break in the curve *BC*, Fig. I.

The 3 : 1 salt can be prepared exactly according to the directions of Wells and Merriam, by dissolving 30 grams of silver thiocyanate and 100 grams of potassium thiocyanate in a small amount of water. Crystals are often obtained several centimeters in length. In the original description of the salt it was mentioned that it turns opaque on standing in the air, and the suggestion was made that it breaks down into another double salt and potassium thiocyanate. It is evident from the solubility experiments that this is what takes place, the salt giving potassium thiocyanate and the 2 : 1 double salt. As this is a very unusual occurrence in double salts, the matter was studied somewhat more closely. Some of the 3 : 1 salt was mixed with potassium thiocyanate and mother-liquor from the double salt and the solubility determined at 25°. The results obtained were:

	Percentage of salt in solution.
KSCN	67.01
AgSCN	9.01

These results agree closely with the results obtained in Experiments 3, 4, and 5, Table I., where a mixture of the 2 : 1 and potassium thiocyanate was present. The 3 : 1 salt gradually turns opaque in the air. Heated in the oven to about 90°, it turns opaque in a few minutes. The transformation was also observed to take place spontaneously when the salt was under the mother-liquor. The white, transformed

area gradually spreads through a large crystal looking like a white fungus growth. By bringing a crystal of the 2 : 1 salt in contact with the 3 : 1 under the mother-liquor the transformation could readily be started. This could not be accomplished by using potassium thiocyanate instead of the 2 : 1 salt. In fact, a crop of the 3 : 1 salt mixed with potassium thiocyanate has been obtained. The crystals of each kind were separated from each other mechanically and analyzed to identify them. The 3 : 1 salt in this case was in large, well-formed crystals, and from its appearance had evidently not changed. When the 3 : 1 salt is shaken with potassium thiocyanate, however, it breaks down, as the solubility results indicate, which were given above.

A solution which had deposited the 3 : 1 salt was further impregnated with a small crystal of the 3 : 1 salt, which had turned opaque. More crystals formed, which were separated from the first crop of 3 : 1, and analyzed. They were found to be the pure 2 : 1 salt, as is shown by the following result :

	Calculated for 2KSCN.AgSCN.	Found.
KSCN	53.92	54.28

The above observations are sufficient to prove conclusively that the 3 : 1 salt is unstable at ordinary temperatures, and passes into a mixture of potassium thiocyanate and 2KSCN. AgSCN. So far as I am aware, no similar case has been observed. It appears to be another illustration of the fact observed by Ostwald[1] that an unstable condition of a system often results in preference to a stable condition.

A transition temperature, above or below which the 3 : 1 salt becomes the stable form, could not be discovered. A large crystal which had begun to change was left out of doors over night under the mother-liquor at a temperature slightly above 0° C. and the transformation progressed steadily. A dilatometer filled with the 2 : 1 salt and potassium thiocyanate and moistened with the mother-liquor saturated with the salts showed no irregular contraction or expansion when cooled to —10° C. If the transition temperature lies below the temperatures investigated, it follows that the reaction

[1] Ztschr. phys. Chem., **22**, 306 (1897).

$$3KSCN.AgSCN = 2KSCN.AgSCN + KSCN$$

takes place with absorption of heat. If the transition temperature is high the reaction takes place with evolution of heat. If this heat effect is appreciable, it could be determined by determining the heat of solution of the 3 : 1 salt before and after it had been transformed.

An attempt was made to do this. The 3 : 1 salt was freed from the mother-liquor between filter-paper and thoroughly air-dried. A part of the crop was then warmed a few minutes at 80° to 90° C. till it turned opaque. The heat of solution of the two products was then determined in a calorimeter, using the same amount of salt in each case and keeping all conditions as nearly alike as possible. The experiment was repeated on a different crop of the salt under somewhat different conditions from those before, but again maintaining the conditions throughout as nearly constant as possible. The following results were obtained :

	Heat of solution of 3KSCN.AgSCN. *a.*	Heat of solution of 2KSCN.AgSCN + KSCN. *b.*	Difference in heat of solution. *b*—*a.*
1	—23.1 Cal.	—22.5 Cal.	+0.6 Cal.
2	—21.1 "	—20.3 "	+0.8 "

The results in the two sets of experiments do not agree very closely, which is perhaps explained by the fact that it is very difficult to obtain the 3 : 1 salt in perfectly pure condition, forming as it does from a mother-liquor containing 70 or 80 per cent of dissolved salts. The difference between the heat of solution of the 3 : 1 salt and the opaque material is very slight, but indicates that the transition temperature lies below the temperatures investigated. This point can hardly be regarded as definitely settled, however.

Summary.

The results in the preceding article may be summarized as follows :

1. A method depending in part on well-known principles of solubility has been devised for determining all the stable double salts formed by two single salts with a common ion at a given temperature.

2. The method has been applied to determine the double thiocyanates of silver and potassium.

3. The double salt, $3KSCN.AgSCN$, has been shown to be unstable under ordinary conditions of temperature, breaking down readily into $2KSCN.AgSCN$ and potassium thiocyanate.

4. It is probable that this unstable salt becomes stable only at a low temperature, if at all.

NEW HAVEN, CONN., February, 1903.

Contributions from the Sheffield Laboratory of Yale University.

CXII.—ON THE DOUBLE CAESIUM AND MERCURIC CHLORIDES AND THEIR SOLUBILITY.

BY H. W. FOOTE.

In the previous article the determination of the double thiocyanates of silver and potassium by means of the solubility of a series of mixtures of the two salts was described. Caesium and mercuric chlorides form one of the largest series of double salts known, and it seemed of interest to apply the method to this series.

The double salts have been described by Wells.[1] They have the following formulas: $3CsCl.HgCl_2$, $2CsCl.HgCl_2$, $CsCl.HgCl_2$, $CsCl.2HgCl_2$, $CsCl.5HgCl_2$. The solubility results have confirmed the existence of these salts, and have shown that others do not exist at the temperature investigated.

The solubility determinations were carried out much as in the previous investigation. An accurately weighed quantity of mercuric chloride was usually treated with a known quantity of water and warmed somewhat, when caesium chloride was added and the mixture warmed in the solubility-tube. The mixtures were then placed in the thermostat at 25°, usually for forty-eight hours. They were rotated about half that time. In only a few cases, where caesium was present in excess, did the mixtures dissolve entirely when warmed. After saturation, a portion of the solution was removed through a pipette closed with a plug of glass wool and, after being weighed, was analyzed as follows: The solution was

[1] Am. J. Sci., 44, 221 (1892).

diluted with cold water, acidified with hydrochloric acid, and treated with hydrogen sulphide. Mercuric sulphide was filtered on a Gooch crucible, dried at 100°, and weighed. The filtrate was evaporated and the residue weighed as caesium chloride. The composition of the residue could then be calculated, and this was done except at the caesium end where the solutions contained a very large excess of caesium chloride. In this case it was found more accurate to analyze the residue. For this analysis the residue was dried as quickly as possible between filter-papers and analyzed by the method already given.

The results are in Table I. Column I. gives the number of the experiment; Columns II. and III., the parts by weight of caesium chloride and mercuric chloride, respectively, in 100 parts by weight of solution; Columns IV. and V., the percentage of caesium chloride and mercuric chloride in the residue; Column VI., the salts present in the residue. The results are separated into groups, each group representing (1) varying composition of the residue and constant composition of solution, where a mixture of two salts is present, or (2) constant composition of the residue and varying composition of solution, showing a pure salt. The results in the latter class, where a pure salt is present, are italicized:

Table I.—Solubility of Caesium and Mercuric Chlorides at 25°.

I.	II. CsCl in solution.	III. $HgCl_2$ in solution.	IV. CsCl in residue.	V. $HgCl_2$ in residue.	VI. Residue contains.
1	*65.61*	*0*	*100*	*0*	CsCl
2	65.71	0.22	95.11	4.89	CsCl and Cs_3HgCl_5
3	65.86	0.21	70.12	29.88	" " "
4	*62.36*	*0.32*	*66.43*	*33.57*	Cs_3HgCl_5
5	*57.01*	*0.64*	*65.96*	*34.04*	"
6	*52.35*	*1.23*	*65.46*	*34.54*	"
7	51.17	1.45	62.86	37.14	Cs_3HgCl_5 and Cs_2HgCl_4
8	51.01	1.43	59.80	40.20	" " "
9	*49.30*	*1.49*	*56.21*	*43.79*	Cs_2HgCl_4
10	*45.95*	*1.69*	*55.47*	*44.53*	"
11	45.45	1.78	48.31	51.69	Cs_2HgCl_4 and $CsHgCl_3$
12	44.99	1.69	39.77	60.23	" " "

Table I.—Solubility of Caesium and Mercuric Chlorides at 25° (*Continued*).

I.	II. CsCl in solution.	III. $HgCl_2$ in solution.	IV. CsCl in residue.	V. $HgCl_2$ in residue.	VI. Residue contains
13	*38.63*	*1.32*	*37.85*	*62.15*	$CsHgCl_3$
14	*27.17*	*0.84*	*37.20*	*62.80*	"
15	*17.03*	*0.51*	*37.60*	*62.40*	"
16	*3.92*	*0.27*	*37.60*	*62.40*	"
17	*1.53*	*0.42*	*37.66*	*62.34*	"
18	0.63	2.66	36.81	63.19	$CsHgCl_3$ and $CsHg_2Cl_5$
19	0.59	2.62	30.99	69.01	" " "
20	*0.49*	*2.91*	*23.43*	*76.57*	$CsHg_2Cl_5$
21	*0.40*	*3.78*	*23.55*	*76.44*	"
22	0.43	4.62	20.46	79.54	$CsHg_2Cl_5$ and $CsHg_5Cl_{11}$
23	0.45	4.65	15.97	84.03	" " "
24	*0.41*	*4.68*	*11.30*	*88.70*	$CsHg_5Cl_{11}$
25	*0.25*	*5.65*	*10.84*	*89.16*	"
26	0.19	7.14	10.62	89.38	$CsHg_5Cl_{11}$ and $HgCl_2$
27	0.20	7.10	9.57	91.43	" " "
28	0.19	7.10	4.93	95.07	" " "
29	0.18	7.06	0.95	99.05	" " "
30	0.17	7.06	0.28	99.72	" " "
31	*0.09*	*7.02*	*0*	*100.0*	$HgCl_2$
32	*0*	*6.90*	*0*	*100.0*	"

Excluding the pure single salts, there are five groups where the residue is very nearly constant in each group, corresponding to five double salts. Table II. gives the calculated percentage of caesium chloride in the five double salts described by Wells. Underneath, the average percentage of caesium chloride in the above residues of each group, corresponding to a double salt, is given :

Table II.

	Cs_3HgCl_5.	Cs_2HgCl_4.	$CsHgCl_3$.	$CsHg_2Cl_5$.	$CsHg_5Cl_{11}$.
CsCl (calculated)	65.10	55.43	38.34	23.72	11.06
CsCl (found)	65.95	55.84	37.58	23.49	11.07

The results in Table II. show conclusively that the salts found were the same as those described by Wells. The possibility of the formation of other stable salts is excluded, as

the differences in composition of the solutions and residues from group to group are but slight.

The results of Table I. have been plotted in Fig. I. The total percentage of dissolved salts has been chosen as ordinate

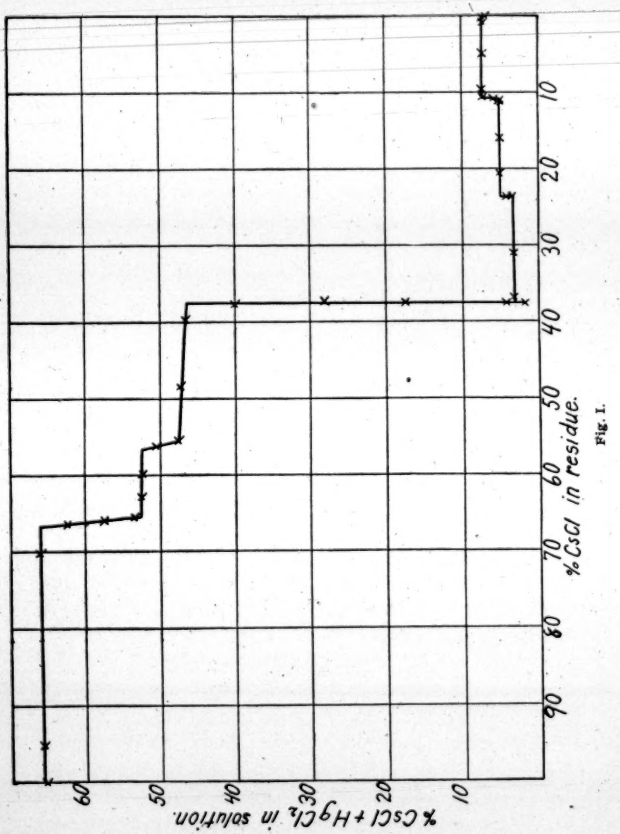


Fig. I.

and the percentage of caesium chloride in the residue as abscissa. The five lines running nearly vertically show nearly constant composition of the residue and variable solubility, corresponding to the five double salts, while each horizontal line represents a mixture of two salts with constant solubility.

Referring back to Table I., it will be noticed in Experiments 13 to 17 where the 1 : 1 salt is present that the amount of mercuric chloride in solution at first diminishes and then increases. The increase is but slight but continues in Experiments 18 and 19, where the 1 : 1 salt is mixed with the 1 : 2 salt. This irregularity would indicate a change in the double salt, but the composition of the residue remains constant. It was noticed by Wells[1] that the 1 : 1 salt occurs in two different crystalline modifications, one form crystallizing in cubes at the caesium end of the series, and the other in orthorhombic crystals at the mercury end. From the results in the table it is evident that the isometric crystals were present in Experiments 13 to 15, and the orthorhombic form in Experiment 17, and possibly in Experiment 16. A change of the crystalline form of a substance is usually associated with a change in temperature, there being but one temperature where both forms are stable. Above and below this temperature only one form can exist. In the present case, at constant temperature, both forms can exist in equilibrium only under one definite set of solubility conditions. Nearer the mercury end the orthorhombic form is stable, while at the caesium end of the series only the isometric form can exist. This conclusion is supported by the phase rule. In case both forms of the double salt were present, there would be four phases in the system, consisting of the two solids, solution and vapor, and three components. The system is thus monovariant. If the temperature be chosen as variable, the concentration of the solution will adjust itself and cannot be varied independently. When one phase disappears the system becomes divariant, and besides the temperature the concentration of the solution may be varied.

The corresponding double bromide, $CsHgBr_3$, is also di-

[1] *Loc. cit.*

morphous,[1] the two forms corresponding to those of the double chloride, and caesium lead bromide, $CsPbBr_3$, occurs in orange-colored and in colorless crystals.[2] In both these cases the two forms can occur at a given temperature, but the relative proportion of the two salts in solution determines which form is stable. Only when the dissolved salts are present in one definite proportion for a given temperature could both salts be stable together. The compound $CsCl_2I$ is also dimorphous[3] and similar influences appear to affect the crystalline form.

Summary.

The results in this article may be summarized as follows:

1. The solubility method of determining double salts, which was devised in the preceding article, has been applied to the double caesium and mercuric chlorides.

2. The five double salts described by Wells were detected and it was shown that no others formed at 25°.

3. The occurrence of two crystalline forms of a double salt at any one temperature was discussed, with examples.

NEW HAVEN, CONN., June, 1903.

THE SOLUBILITY-CURVE OF SODIUM TETRABORATE.

BY D. W. HORN AND ELIZABETH M. VAN WAGENER.

The following paper is based on volumetric analyses of saturated solutions of borax, prepared from both supersaturated and unsaturated solutions, at a number of temperatures between 0° and 100°.

The well-defined, crystalline hydrates of sodium tetraborate have been known for a long time. The one, the decahydrate, $Na_2B_4O_7 + 10H_2O$, as "ordinary," "monoclinic," or "prismatic borax,"[4] and the other the pentahydrate, $Na_2B_4O_7 + 5H_2O$, as "octahedral borax."[5] These hydrates can be ob-

[1] Wells: Am. J. Sci., 44, 228 (1892).

[2] Walden: *Ibid.*, 45, 128 (1893).

[3] Wells: *Ibid.*, 43, 26 (1892).

[4] Known to early chemists; composition determined 1747 by Baron; used by Berzelius in determining atomic weight of boron.

[5] Discovered by Payen, 1829; Jsb., 8, 171; Ding. polytech. J., 26, 231.

tained from the same solution,[1] and in the solid form the decahydrate passes into the pentahydrate when it is heated.[2] From these facts an irregularity in the solubility-curve of sodium tetraborate is to be expected, for, repeatedly, experiment has shown that a change in the degree of hydration of a salt and a change in the direction of the solubility-curve of that salt (in water as a solvent) are interdependent.[3]

According to the data from the measurements of the tension of water-vapor over borax, the temperature at which the transition of the decahydrate into the pentahydrate is complete is 60°.[4] An irregularity should occur in the solubility-curve at the point corresponding to this temperature. However, when the solubility of sodium tetraborate, as determined by Poggiale,[5] is represented in graphic form, the resulting curve undergoes no sudden change in direction throughout its course. In fact it is quite similar (see figure) to that of potassium chlorate,[6] of which no hydrates are known. Since no irregularity occurs, the curve and the corresponding behavior of the system must be considered exceptional, or the data must be assumed to be insufficient or erroneous.

Consideration of Poggiale's method does not lead one to expect great errors, but small ones would be difficult to avoid. Assuming that the errors are not great and that an irregularity at 60° would appear in the curve had enough determinations

[1] Gernez, 1874: Compt. rend., **78**, 68; Payen, 1843: Jsb., **22**, 147; Ann. chim. phys., [3], **8**, 353; Arzruni, 1876: Jsb., 1876, p. 224: Pogg. Ann., **158**, 250.

[2] Lesceour, 1896: Ann. chim. phys. [7], **9**, 545.

[3] Ostwald: "Solutions" (tr. by Muir), p. 75.

[4] The idea that 56° is the lower temperature limit for the existence of the pentahydrate probably originated in Payen's statement that when borax is dissolved in boiling water until the specific gravity of the solution becomes 1.246, the pentahydrate separates, on cooling, between 79° and 56°; and below 56°, the decahydrate. This temperature limit in a solution of one definite concentration is quite a different thing from the lowest temperature at which the pentahydrate can exist in equilibrium with its saturated solution. In fact, Gernez has shown that the pentahydrate crystallizes spontaneously from the proper supersaturated solutions at temperatures as low as 8°.

Lesceour's measurements show that at ordinary temperatures the pure decahydrate is stable, not having over it a measurable tension of water-vapor. With rising temperature the tension rises quite rapidly until 60° is reached, when it falls again below the measurable limit. Evidently at 60° the decahydrate ceases to exist. At this temperature the new hydrate formed is stable. Lesceour proved it to be the pentahydrate.

[5] Ann. chim. phys. [3], **8**, 467 (1843).

[6] Etard: Compt. rend., **108**, 177 (1889).

of solubility at temperatures near 60° been made, the curve is still exceptional and remarkable in that, though it is a compound curve, its two parts have so nearly the same direction and curvature as to form a continuous curve when joined together. In this respect the curve is unlike the larger number of those of salts having more than one hydrate within the same limits of temperature as the curve is plotted. Interpreted in accordance with the accepted ideas, this must mean that, except about 60°, the two different hydrates of sodium tetraborate approximate quite nearly to having the same heat of solution in its saturated solution. Our knowledge of the act of solution does not contradict the possibility of this, but our knowledge of a large number of other cases in point[1] warrants us in not expecting two entirely different substances to be exactly alike in this one property.

As a result of these considerations, we have determined the solubility of sodium tetraborate with the view of testing the sufficiency and accuracy of the data given by Poggiale. His method consisted in evaporating saturated solutions of borax to dryness and weighing the residues after complete dehydration. Troublesome frothing accompanies this procedure, and his practice was to puncture the films in the froth with a glass point to release the imprisoned steam. Unless the temperature is carefully regulated, the salt is often thrown out with considerable force and the crucible, in which the experiment is being carried out, broken. We adopted a method that avoids evaporations to dryness. We have determined the sodium tetraborate in weighed quantities of the saturated solutions by titration (after dilution) with standard acid, using methyl orange as indicator.

The following table contains the averages of our analyses. For comparison, Poggiale's data are also given. The numbers represent the solubility expressed as the number of grams of sodium tetraborate (anhydrous borax) dissolved by 100 grams of water. The figures in the column marked "U" were obtained by analyses of saturated solutions prepared from unsatu-

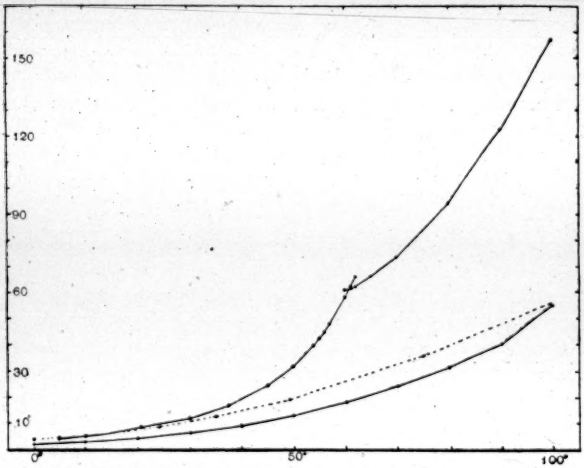
[1] Ztschr. phys. Chem., **5**, 198 (1890); Compt. rend., **98**, 993, 1276, 1432 (1884); **104**, 1614 (1887); **106**, 206, 740 (1888); Ann. chim. phys. [5], **30**, 411 (1883); J. Chem. Soc. (London), Feb., 1903 (barium acetate); and many other cases.

rated ones, an excess of the salt remaining in contact with the solution after saturation; the figures in the column marked "S," by analyses of saturated solutions prepared from supersaturated ones. The supersaturated solutions were filtered beforehand and the experiment so conducted as to insure crystallization at or very near the temperature at which the solubility was desired.

Temperature, C.	U.	S.	Average.	Poggiale's data.
0°				1.5
5°	1.3	1.4	1.3	
10°		1.6	1.6	2.4
20°				4.0
21°.5	2.8	2.8	2.8	
30°	4.0	3.9	3.9	6.0
37°.5	5.6	5.7	5.6	
40°				8.8
45°	8.1	8.1	8.1	
50°	10.4	10.6	10.5	12.9
54°	13.3	13.3	13.3	
55°	14.1	14.3	14.2	
56°	15.0	15.0	15.0	
57°	15.9	16.0	16.0	
60°	19.4	20.3		18.1
61°	20.7	20.4		
62°	22.0	20.7		
65°	22.0	21.9	22.0	
70°	24.5	24.4	24.4	24.2
80°	31.3	31.5	31.4	31.2
90°	40.7	41.0	40.8	40.1
100°	52.2	52.5	52.3	55.2

The relations between the data obtained at temperatures from 60° to 65° are different from those in other cases. The solubility as determined in solutions made from unsaturated solutions does not increase when the temperature is raised from 62° to 65°, and the increase in solubility for each degree from 60° to 62° is of a much smaller order than that for each degree from 54° to 57°. At 60° there is a considerable difference in the solubility depending on whether the experiment was begun with an unsaturated or a supersaturated solution, but the general rule that a greater value is gotten when a supersaturated solution is used for the preparation of the saturated solu-

tion holds good. At 61° and 62°, however, there is a reversal of this relation. The curve offers an interpretation for these results.



Lower curve, Poggiale's curve for sodium biborate; dotted curve, curve for potassium chlorate; upper curve, new curve for sodium biborate. In the upper curve the ordinates have each been changed to a different value to bring out more clearly the relations; ordinate = 3 × solubility.

We believe we have here to deal with meta-stability in the two hydrates. That of the decahydrate is the better defined. The values for the point on its curve at 62° were, after two and three hours, respectively, 22.02 and 21.92. On the other hand, the values for the point on the curve of the pentahydrate at 60° were 20.29 and 20.15 after two hours, and 19.80 and 19.79 after three hours. We believe this fall in solubility to be due to a transition (but partial, after three hours) of the pentahydrate into the decahydrate. At 61°, however, the pentahydrate is stable, the values for the point on its curve at this temperature being, after two and three hours, respectively, 20.48 and 20.31.

There is no evidence to be found in this curve, nor in the measurements of Lesceour, pointing to the existence of the hexahydrate, $Na_2B_4O_7 + 6H_2O$, described by Biechi,[1] as an incrustation at the Tuscan lagoons.

Details of Experiments.

In this work we used a water-bath of the type used and described by A. A. Noyes,[2] the shaft being turned by a small hot-air engine. Iron burette-clamps were so arranged on the shaft that two bottles of about 200 cc. capacity each could be firmly and quickly attached to it, and as quickly removed from it. The bottles were closed with rubber stoppers, well tied in. A thermometer with a long scale of about 115° was used. By constant attention and the use of hot and cold water and an extra burner it was possible to keep the temperature of the water in the bath constant within $\pm 0°.1$. Each experiment lasted from four and a half to six hours. Two hours after the temperature had been adjusted and the shaft with bottles attached set in motion, the bottles were removed from the clamps on the shaft, the fastenings on the stoppers and the stoppers themselves loosened, and the bottles (loosely stoppered) fastened at the sides of the bath until the liquid in them was clear, all suspended matter having settled. This required from one-half to one and one-half hours, depending on the elevation of the temperature. When clear, specimens of the solutions were taken for analysis, the bottles closed, returned to the shaft, agitated for one hour more, and specimens taken again just as before. Two hours were sufficient for the point of saturation to be reached. The agitation for a third hour did not change the value for the solubility.

Some of the saturated solution was permitted to flow out from the bottle in such a way as to rinse its neck and lip, before the specimens for analysis were poured from it. The specimens were poured directly from the bottle into weighing-tubes provided with glass stoppers, the weight of each with its stopper having been determined just prior to the experiment. The stoppers were closed at once to prevent loss by evaporation,

[1] Am. J. Sci., [2], 17, 129; 19, 120; Jsb., 1854, p. 867.
[2] Ztschr. phys. Chem., 9, 606 (1892).

and when cold the tubes and contents were weighed and transferred to beakers containing hot water, in which all salt that had crystallized out dissolved. When the contents of the beakers were cold they were titrated with standard sulphuric acid, using methyl orange as indicator.

The unsaturated solutions were made by putting the decahydrate in contact with water, in quantities but little more than sufficient to saturate the water. The supersaturated solutions were made at temperatures about 10° above that of the corresponding experiment, and were filtered through a hot funnel into the bottle, which was immersed in a water-bath at the same temperature as that at which the solution had been made. The bottle was tightly stoppered before it was removed from this bath, and then transferred quickly to the large (solubility) bath, the temperature of which was from 1° to 2° higher than that at which the solubility was to be determined. When the bottles had been attached to the shaft and it had been started in motion, the temperature of the water of the bath was quickly reduced to that desired for the experiment by the cautious addition of cold water. In this way it was assured that crystallization took place at or very near the temperature at which the solubility was being determined.

The borax used was "refined" borax recrystallized from water till its solution showed no trace of $\overline{\overline{SO}}_4$ or $\bar{Cl}$ when properly tested. The sulphuric acid was approximately N/5, and had been standardized by pure potassium tetroxalate and by pure borax, the standardizations being made by two different persons and checking up quite closely with each other.[1]

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June 1, 1903.

REVIEWS.

THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY. By R. A. WITTHAUS, A.M., M.D., Professor of Chemistry, Physics, and Toxicology in Cornell University Medical College, New York City. Fifth edition. New York: William Wood & Co. 1902. pp. 678.

The edition has about the same scope as the previous one. It is intended to be used by medical students as a manual for

[1] Standardized by tetroxalate, 1 cc. contained 0.009577 gram of H_2SO_4; by borax, cc. contained 0.009584 gram H_2SO_4.

inorganic, organic, and physiological chemistry. The part on organic chemistry has been in great part rewritten and somewhat extended. Covering as it does so much ground it is well-nigh impossible to present the material in a perfectly satisfactory way within the space allotted.

In the section on organic chemistry, more could perhaps be gained by omitting the description of many compounds that have at present no medical bearing, and paying more attention to the methods of determining the structure of a few typical compounds and thus conveying a clearer idea of what is meant by structural formulas. The latter 117 pages are devoted to physiological chemistry. The part dealing with the enzymes is entirely too brief when it is remembered that the book is intended for medical students, and it has not kept pace with the recent work in this field. For instance, the old distinction between formed and unformed ferments has hardly a place in a modern text-book and has been of little more than historical interest since Buchner's isolation of zymase in 1897. There is no justification for referring to the catalytic activity of enzymes as "false fermentations" (p. 243). In many places the style is not very clear and the meaning involved. A few errors have crept into the text, such as on p. 345, the formula for potassium ferrocyanide is given as $Fe\begin{matrix}C_3H_3K_2\\C_3H_3K_2\end{matrix}$, etc.

Throughout the book especial emphasis is placed upon those substances of toxicological interest and on the reactions used in toxicology. The great development of the chemical aspect of the medical sciences in recent years renders it the more urgent that the chemical training of the medical student be more comprehensive and fundamental in character, and attempts to teach inorganic, organic, physiological, and clinical chemistry from a single book should be discouraged. Such attempts must necessarily be barren of results, and can only retard the growth of the chemical aspect of medicine.

A. S. L.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By DR. H. MEYER, Docent and Adjunct of the Imperial and Royal German University, Prague. Translated by J. BISHOP TINGLE, PH.D., F.C.S., Professor of Chemistry at Illinois College, Jacksonville, Illinois. Second edition, rewritten. 12mo. pp. xii + 162. New York: John Wiley & Sons. 1903.

The first edition of this book was reviewed in this JOURNAL[1] soon after its appearance. Its usefulness "has been shown

[1] This JOURNAL, 23, 451 (1900).

by the comparatively quick exhaustion of the first edition. The present issue has been thoroughly revised by Dr. Meyer and the writer, the whole work has been reset, and more than 20 per cent of new matter has been added, including several figures." Several new methods have been given, especially for the determination of alkyls, carbonyl, and the nitroso and methylene groups. It is believed that the book in its present form will prove even more generally useful than the first edition. C. E. W.

DER STICKSTOFF UND SEINE WICHTIGSTEN VERBINDUNGEN. By DR. LEOPOLD SPIEGEL, Privatdocent an der Universität Berlin. Braunschweig: Friedrich Vieweg und Sohn. 1903. 909 Seiten. Geheftet, 20 Mark; gebunden, 22 Mark.

This book is intended to bring together in convenient form an account of the more important compounds of the element nitrogen in order to facilitate the work of those who would otherwise be obliged to search through many journals and books to get a clear idea of the general relationships of their own particular field to the entire group of nitrogen compounds. It is intended to play the part for these that "Beilstein" does for the carbon compounds. The references to the literature are given as foot-notes, and the constants in tables that follow the text proper, in which the methods of preparation and other information are set forth. Thus, there are 18 pages of text devoted to the amines, imines, acid amides, amidines, and similar compounds. Following this are 79 pages of tables in which are given the names, formulas, melting- and boiling-points, and specific gravities of these substances. Sixteen pages of tables with similar information are given to the alkaloids, and the names of their discoverers and the sources from which they are obtained are also stated.

Among other general subjects the following are discussed: Nitrogen, the halides, oxides, sulphides, and hydrides of nitrogen, the nitrides, the cyanogen derivatives, nitrogen in closed rings, the alkaloids, the proteids, analytical methods, etc. The book is well printed, its arrangement is good, and it should prove of great value to all chemists, in spite of one or two minor points in which an improvement might be suggested. C. E. W.